QUALITATIVE
ORGANIC CHEMISTRY

QUALITATIVE ORGANIC CHEMISTRY

BY

NEIL CAMPBELL

LECTURER IN ORGANIC CHEMISTRY,
UNIVERSITY OF EDINBURGH

MACMILLAN AND CO., LIMITED
ST. MARTIN'S STREET, LONDON
1946

PREFACE

The aim of this book is to present the principles of qualitative organic analysis and to give some idea of the methods used in examining organic compounds. The book is intended primarily for students taking a course in qualitative work, but it is also hoped that it may be helpful to advanced students and research workers. The book is essentially a laboratory guide, but, as it is important that students should understand fully the chemical basis of the methods used, an explanatory chapter has been included.

Many schemes have been advanced for the systematic identification of organic compounds. The methods used in this book are based mainly on the chemical properties of organic compounds, although physical characteristics have also been utilised. An attempt has been made to make the scheme as complete as possible without being cumbrous, but it is realised that no rigid scheme is sufficient to meet all the demands of qualitative analysis, and a book of this kind serves its purpose only in so far as it assists the student to apply his knowledge and initiative to the problems before him.

The choice of reagents has not been an easy matter, as many which are the first choice of the research worker are, for one reason or another, unsuitable for students in a large class. For this reason expensive chemicals and apparatus have been omitted. The tests given have been chosen so that they can be performed in a short time on small quantities of substances.

Considerable attention has been paid to the preparation of derivatives. Not only is this the most satisfactory method of identification, but the preparation and purification of small quantities of substances form an essential part of the organic chemist's training. During the preparation of the book the author has taken the opportunity to investigate carefully the merits of

identification derivatives, and to check their melting points, so as to make the book as accurate and as reliable as possible. Only those derivatives which are readily prepared in the pure state have been included. Many tests and derivatives commonly included in text-books have been found unsatisfactory, at least for students, and have been omitted. On the other hand, many of the reagents recently introduced, especially by American workers, have proved to be of great value, and are described in the text.

The boiling points and melting points quoted in Part B have been obtained from the most reliable sources available, such as recent papers dealing with highly purified compounds, and in the majority of cases have been checked in the author's laboratory.

In order that students may acquire the habit of consulting the original literature and standard works, references and a bibliography are given.

It is impossible to acknowledge all the sources of information used in making this book. Free use has been made of the books quoted in the bibliography and of the chemical journals.

The author wishes to thank Dr. Nora Campbell for preparing the diagrams; Dr. H. G. Rule for reading the manuscript and for many valuable suggestions; Dr. E. G. V. Percival for advice and criticism; and Professor L. C. Raiford of the State University of Iowa, U.S.A., for the use of the plate for diagram 1.

Finally he wishes to express his indebtedness to those students in Duke University, U.S.A., and Edinburgh University who so willingly co-operated in testing methods and reagents.

The author will be grateful for information regarding any errors and inaccuracies which may be found in the book.

Edinburgh,
September 1938.

ABBREVIATIONS USED IN THE REFERENCES

Abbreviation.	Full Title.
Analyst . . .	*The Analyst.*
Ber.	*Berichte der deutschen chemischen Gesellschaft.*
Biochem. J. . .	*Biochemical Journal.*
Centr. . . .	*Chemisches Zentralblatt.*
Helv. Chim. Acta. .	*Helvetica Chimica Acta.*
J.	*Journal of the Chemical Society.*
J. Amer. Chem. Soc. .	*Journal of the American Chemical Society.*
J. Org. Chem. . .	*Journal of Organic Chemistry.*
Ind. Eng. Chem. (Anal.)	*Journal of Industrial and Engineering Chemistry.* Analytical Edition.
J. Chem. Educ. . .	*Journal of Chemical Education.*
Mikrochem. . .	*Mikrochemie.*
Monatsh. . . .	*Monatshefte für Chemie.*
Rec. trav. chim. . .	*Recueil des travaux chimiques des Pays-Bas et de la Belgique.*

CONTENTS

PART A

INTRODUCTORY CHAPTER

Most organic compounds are not appreciably ionised in solution, and consequently some method other than that used in qualitative inorganic chemistry must be adopted for their detection and identification. The method used consists in determining the chemical and physical properties of the compound under examination, and then consulting reference books to find a compound with identical properties. For example, an "unknown" compound containing carbon, hydrogen, and oxygen is found to be an acid; to contain a phenolic group; and to melt at 159°. From the literature it is found that salicylic acid has all these properties, and therefore the compound is probably that acid. The compound is then completely identified by other specific tests.

The complete examination of a compound involves four stages.

1. Purification of the sample, if necessary.
2. Preliminary tests. The compound is classified, for example, as a hydrocarbon, aromatic acid, etc., and is identified by its physical properties.
3. Supplementary tests. These are often applied to confirm the preliminary tests.
4. Preparation of crystalline derivatives and determination of their melting points.

Part A of this book outlines the methods used in qualitative work, while Part B is a reference section giving data for the identification of some hundreds of common organic compounds.

It should be stressed that this book is not intended to give any hard-and-fast rules, but merely serves to introduce the student to the apparatus, reagents, and methods used in

qualitative organic work. Each compound given for identification should be regarded as a problem which can be solved partly by following a routine procedure and partly by application of the student's own knowledge and power of observation. Thus the student with crystallographic knowledge will be able to identify some of his " unknowns " by means of the polarising microscope, and the student with biochemical experience will use certain tests not given in this book. Further, by consulting larger books on the subject, such as Mulliken's *Identification of Pure Organic Compounds*, or the orginal papers in the chemical journals, he will be able to appreciate better both the scope and the limitations of the methods used. Only if such limitations are realised is it possible to attack qualitative work confidently and avoid frequent failure. For instance, it is not sufficient to know that picric acid is an excellent reagent for giving crystalline derivatives with aromatic hydrocarbons, but it must be realised that, as in the case of benzene, some of the picrates are too unstable to be isolated under ordinary conditions. Efforts to identify benzene by use of picric acid are therefore doomed to failure. The cultivation of a critical faculty and a sense of discrimination is not the least important part of the organic chemist's training.

CHAPTER I

PURE COMPOUNDS. ISOLATION AND CRITERIA OF PURITY

BEFORE examining an unknown compound, it is first necessary to discover its degree of purity. The appearance of the sample is often sufficient to show that it is impure, but generally it is necessary to make use of physical properties such as the melting point, boiling point, density, etc.

Most crystalline organic compounds when they are pure have definite melting points. A substance may, therefore, be considered pure enough for all practical purposes if it has a homogeneous appearance under the microscope and melts over a range of not more than one or, in some cases, two degrees (capillary-tube method). To check the purity of a compound after determining its melting point, it is advisable to recrystallise it from a suitable solvent and re-determine its melting point. If this is not altered, the compound is regarded as pure.

Substances such as sulphanilic acid present difficulties, as they have no definite melting-point, and are not readily obtained in the crystalline state. Various procedures may be adopted. The compound may be boiled in a solvent in which it is insoluble, in the hope that impurities will be extracted. The more general method, however, is to convert it into a derivative which is easily purified. Thus terephthalic acid has no definite melting point, but may be easily converted into its methyl ester, which crystallises from ethyl alcohol and has a definite melting point. The purity of the ester may therefore be checked, and the acid regenerated from it by hydrolysis. The purity of acids may also be tested by determination of their neutralisation equivalents. Metallic salts of organic acids have no definite melting-point, but often, especially in the aromatic series, the parent acid can be isolated in the solid state by addition of a mineral acid to an aqueous solution of the salt.

Every pure liquid has a characteristic temperature called the boiling point, at which its vapour pressure is equal to that of the atmosphere. At the boiling-point ebullition sets in, and the liquid distils. As the boiling-point is so characteristic and easily determined, it is an important aid in the identification of liquids.

In addition to the melting-point and boiling-point, other physical constants are of value in determining the purity of compounds. Those most frequently used are the density or specific gravity, neutralisation equivalents of acidic compounds, refractive index, and the specific rotation of optically active compounds. In the case of liquids which do not yield crystalline derivatives easily, it is advisable to obtain at least two physical constants for identification.

This chapter deals with the examination of the physical properties of compounds and their purification.

Examination under the Microscope

The substance to be examined is recrystallised from a suitable solvent, and a drop of the liquid containing the suspended crystals is placed on a slide glass, and immediately examined under a microscope of magnifying power 50—100. The colour and crystalline appearance are noted, and the form of the crystals may be described in detail, especially if a polarising microscope is available (see *Crystals and the Polarising Microscope*, by Hartshorne and Stuart). Generally this is not done, and it is sufficient to describe the crystals as prisms, needles, hexagonal plates, etc., though with a suitable microscope it is possible to determine the profile angles of crystals, and thus characterise compounds more completely (cf. Shead, *Ind. Eng. Chem.* (*Anal.*), 1937, **9**, 496). Urea nitrate, for instance, can be identified in this way.

From the microscopic examination it is possible to see whether or not compounds are pure, since mixtures are readily detected in this manner.

An excellent example of the use of the microscope is found in a paper by Raiford and Peterson (*J. Org. Chem.*, 1937, **1**, 544). The phenylhydrazones of substituted chalkones are isomeric with the triphenylpyrazolines, and often rearrange spontaneously

to give the latter. The isomers are most easily distinguished by microscopic examination, as is clearly shown by a consideration of Fig. 1, which gives the crystalline appearance of a typical pair of isomers under the microscope.

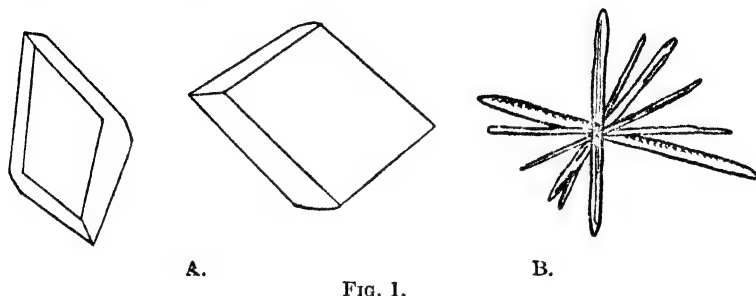



FIG. 1.

A. Phenylhydrazone of 4′-chlorochalkone.
B. 1 : 5-Diphenyl-3-(4-chlorophenyl)pyrazoline.

Melting Point Determination

Many types of apparatus are available for the determination of melting points of small quantities of substances in capillary tubes. Two of the simplest are described.

A 100-c.c. beaker is two-thirds filled with mineral oil or concentrated sulphuric acid, though the latter is somewhat dangerous. The bulb of a standardised thermometer (see p. 8) reading to 250° or 300° is placed in the oil bath, which is stirred by means of a glass rod bent into a suitable shape (Fig. 2). A capillary tube of the size shown in Fig. 2 is made by heating ½-in. tubing in a blow-pipe flame, and drawing it out to give a length of thin-walled capillary tubing which can be cut into several melting point tubes. The melting capillary is sealed at one end, and is filled to a height of 2 mm. with the compound, which has been thoroughly dried on a piece of porous plate. The capillary is best filled by introducing the compound at the top of the tube, and transferring it to the bottom by drawing a round file gently across the tube. The tube is then attached to the thermometer by moistening it with the bath liquid and gently pressing it against the thermometer. The bath is heated and stirred continuously

until a certain temperature is reached at which the compound is seen to melt, the temperature recorded giving an approximate value for the melting point. The bath is allowed to cool to about ten degrees below the approximate melting point, and the melting point is accurately determined on a fresh sample by raising the temperature of the bath slowly—about one degree per 30 seconds. The temperatures at which the compound begins to melt and at which liquefaction is complete are noted. This range is quoted as the melting point, and gives an indication of the purity of the compound. For pure compounds it should not exceed 0·5°, but many chemicals encountered in the laboratory melt over a larger range. Many compounds soften or **sinter** below their melting points without forming any liquid.

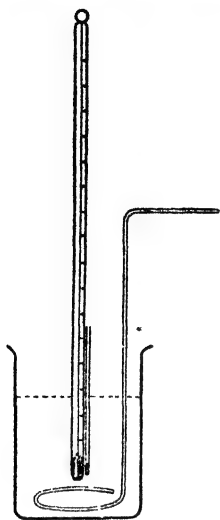



Fig. 2.

Hand blow-pipes make efficient micro-burners suitable for obtaining a very slow increase in the temperature of the bath (Fig. 3), the flame being protected from draughts by a piece of Pyrex glass tubing.

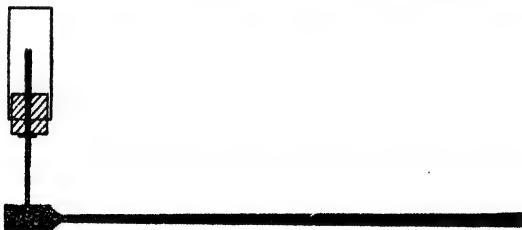



Fig. 3.

In the second type of apparatus made of Pyrex glass the bath

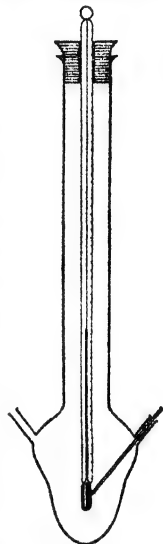
is so shaped that the liquid is stirred by convection currents (Fig. 4). A capillary tube, constructed and filled as outlined above, is inserted in one of the side-arms of the apparatus so that its sealed end is near the bulb of the thermometer. The melting point is determined in the same way as with the first apparatus, and reliable melting points can be obtained. Dibutyl phthalate may be used as the bath liquid in this apparatus (Brown, *J. Chem. Ed.*, 1937, **14**, 380).

The electrically heated apparatus of Mason (made by Gallenkamp) is very suitable for substances melting between 250° and 400°.

The capillary-tube method does not give true melting points, slightly higher values being obtained. Thus Reissert (*Ber.*, 1890, **23**, 2239) found that the melting point of a sample of *m*-dinitrobenzene determined by the capillary-tube method had a value of 89·95°, in comparison with a value of 88·75° obtained by a more reliable method. Another drawback of the method is the difficulty sometimes found in obtaining sharp melting points even of very pure compounds. For qualitative purposes, however, the method is excellent, and most of the melting points quoted in the literature and this book are obtained in this way. For the determination of true melting points Mulliken's *The Identification of Pure Organic Compounds* and the *Journal of the Chemical Society*, 1936, p. 137, should be consulted.

FIG. 4.

Many substances, such as phthalic acid, which decompose on heating have different melting points, according to the conditions used in making the determination, and in these cases it is advisable to raise the temperature of the bath nearly to the melting point of the substance before introducing the capillary tube.

Two samples submitted for examination, if found to have the same melting points, may or may not be identical. This is easily determined by the **method of mixed melting points.** Equal quantities of the samples are ground together, and the

melting point of the mixture is determined. If the melting point of the mixture is the same as that of the samples, the compounds are identical. If, on the other hand, the melting point is lowered by ten or more degrees, the compounds are not identical. Occasionally the conclusions drawn from this method of mixed melting points cannot be relied upon (see, for example, *Ber.*, 1935, **68**, 1200).

With suitable apparatus it is possible to determine the melting points of compounds when only microscopic quantities are available (see Kofler and Kofler, "*Mikroskopische Methoden in der Mikrochemie*").

Calibration of Thermometers

Generally the thermometers used in the laboratory read up to 250 or 300°, and must be calibrated, as they are frequently inaccurate, especially at higher temperatures. "Stem corrections" are often applied, as the entire length of the mercury column is not at the same temperature as that of the bulb. This correction is given by $N\ (T - t) \times 0{\cdot}000154$, where $N =$ number of degrees of the mercury column which is exposed, $T =$ the observed temperature, and $t =$ the average temperature of the mercury column, and is added to the temperature observed. The method is, however, open to certain serious objections, and it is advisable to calibrate the thermometer in one of the following ways.

1. *Calibration against standard short-stem Thermometers.*

The thermometer and the standard thermometer are placed side by side in the apparatus shown in Fig. 2, and comparisons are made at intervals of five degrees between the thermometers as the temperature of the bath is increased. The necessary corrections are then made and noted either in a record-book or on a label attached to the thermometer. For ordinary work it is only necessary to calibrate thermometers to the nearest degree. The following table gives the calibration of a 300° Jena glass thermometer.

Table

Standard thermometer.	Thermometer.	Correction.
48°	50°	—2°
53	55	—2
58	60	—2
63	65	—2
68	70	—2
73	75	—2
78	80	—2
83	85	—2
89	90	—1
94	95	—1
99	100	—1
104	105	—1
109	110	—1
114	115	—1
119	120	—1
124	125	—1
129	130	—1
134	135	—1
139	140	—1
145	145	0
150	150	0
155	155	0
160	160	0
165	165	0
170	170	0
176	175	+1
182	180	+2
187	185	+2
193	190	+3
203	200	+3
208	205	+3
213	210	+3
218	215	+3
224	220	+4
229	225	+4
235	230	+5
240	235	+5
246	240	+6
252	245	+7
257	250	+7

2. *Calibration by Determination of the Melting or Boiling Points of Pure Compounds.*

The melting points or boiling points of six or eight compounds are determined, and from the known constants of the compounds the thermometer can be calibrated. It need scarcely be empha-

sised that the compounds used must be absolutely pure. An example of this method of calibration is given in the following table.

Table

Compound.	True m.p.	M.p. obtained.	Correction.
Diphenylamine	54°	56°	—2°
Naphthalene	80	82	—2
Benzoic acid	122	123	—1
Salicylic acid	159	159	0
p-Toluic acid	178	176	+2
Anthracene	217	214	+3
p-Bromobenzoic acid	254	247	+7

The following compounds are suitable for calibration purposes.

Liquids.	B.p.	Solids.	M.p.
Chloroform	61°	Diphenylamine	54°
Ethyl iodide	72	*o*-Nitraniline	71
Water	100	Naphthalene	80
Toluene	111	*a*-Naphthol	94
Chlorobenzene	132	Benzoic acid	122
Bromobenzene	156	Benzoin	137
Aniline	184	Salicylic acid	159
Nitrobenzene	211	*p*-Toluic acid	178
Quinoline	239	3 : 5-Dinitrobenzoic acid	204
a-Bromonaphthalene	281	Anthracene	217
		p-Bromobenzoic acid	254

Boiling-Point Determination

It is generally advantageous to distil any liquid under examination in order to obtain it in the pure state before proceeding to the detailed analysis.

For small quantities of liquid the apparatus shown in Fig. 5 is convenient and efficient. The 10-c.c. flask, which should never be more than two-thirds full, is fitted with a thermometer the bulb of which is situated just at the outlet arm. If the liquid boils above 120°, an air condenser is attached, otherwise a small 6-in. water condenser is used. The flask is gently heated, and the temperature as shown by the thermometer soon begins to rise quickly until it reaches a stationary point at which

most of the liquid distils over. This is the boiling-point. The main fraction should distil over a range of not more than one or two degrees.

Some liquids do not boil until heated above their boiling-points, and are said to be **superheated.** They boil very unsteadily, and "**bumping**" occurs, making distillation difficult. Bumping may be avoided, or at least moderated, by the introduction of a few pieces of porous tile *before* the distillation.

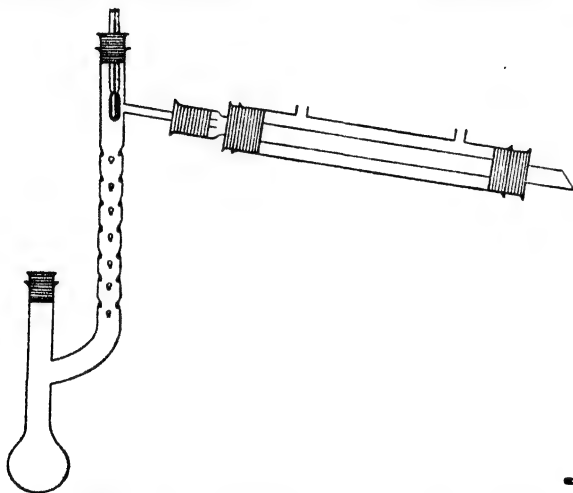
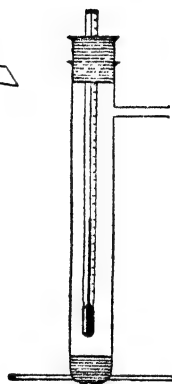
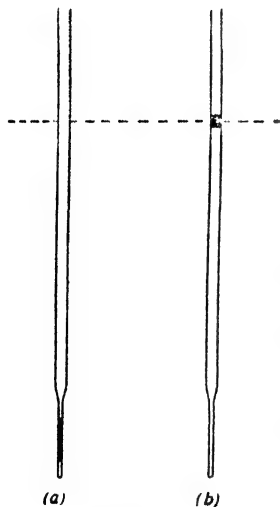



Fig. 5. Fig. 6.

With smaller quantities of liquid the boiling-point may be determined with the apparatus shown in Fig. 6. This consists of a Gooch filter tube resting on an asbestos sheet with a hole in it. A small volume of the liquid (about 1 c.c.) and a piece of porous plate are introduced into the tube and a thermometer is inserted. When the liquid boils, the thermometer registers the boiling-point. The apparatus cannot be used for volatile inflammable liquids such as ether.

A very neat micro-method is frequently employed. The end of a capillary tube such as that used for melting point determinations is drawn out in a micro-flame to a very fine capillary about 1 cm. long. The end of this capillary is immersed in a drop of the

liquid for about 20 seconds, and is then sealed off in a micro-flame (see p. 6). In this way a small quantity of the liquid is drawn into the capillary and a small bubble of air is enclosed in the extreme tip of the tube (Fig. 7a). The capillary tube is attached to the thermometer of the melting-point apparatus (p. 6), and as the bath is heated the drop of liquid rises in the capillary tube. When it reaches the surface of the liquid (Fig. 7b), the temperature is noted. This is the boiling-point.

(a) (b)
Fig. 7.

Density and Specific Gravity

The density of a substance is defined as the mass in grammes of one cubic centimetre of the substance, and its value naturally varies with the temperature. The specific gravity of a substance is defined as the ratio of the weight of a given volume of the substance at a given temperature to the weight of the same volume of water at the same or a different temperature. It is denoted by the letter *d*. Thus d_{25}^{25} indicates the specific gravity of the substance at 25° C., referred to water at 25° C.; d_4^{20} indicates the specific gravity of the substance at 20° referred to water at 4° C. Since 1 c.c. of water at 4° C. weighs 1 gramme, it follows that d_4^{20} is simply another way of expressing the density of the substance at 20° C.

Density measurements are most frequently used along with refractive index measurements to determine the purity of liquids. It is necessary to make accurate measurements under carefully controlled temperature conditions. This is done by means of pyknometers and thermostats (see Findlay's *Practical Physical Chemistry*). For qualitative work densities are sometimes determined by weighing a known volume of liquid delivered from a pipette, but only approximate values are obtained by this method.

Refractive Index

The refractive index, generally denoted by the letter n, is dependent on the wave-length of the light used and to a smaller degree on the temperature. The sodium D line and a temperature of 20° C. are commonly used, as indicated by the symbol n_D^{20}. The most convenient instrument for determining refractivities in qualitative work is the Abbé refractometer.

Specific Rotation

The specific rotation is denoted by $[\alpha]$, and is dependent on the wave-length of the light used, on the temperature, and on the solvent, if any, employed. It is given by the formula

$$[\alpha] = \frac{100 \times \alpha}{l \times c}$$

where α represents the observed angle of rotation, l the length of the polarimeter tube in decimetres, and c the weight in grammes of substance in 100 c.c. of solution. The sodium line or the mercury green line (5461) are most commonly used. $[\alpha]_D^{20}$ denotes the specific rotation at 20° observed with sodium light.

Neutralisation Equivalent

The neutralisation equivalent of an organic acid or acidic compound such as 2 : 4 : 6-tribromophenol can be quickly determined. About 0·2 g. of the compound is weighed accurately, dissolved or suspended in water, and titrated against N/10 sodium hydroxide solution, phenolphthalein being used as indicator. The equivalent is the weight of the compound which neutralises 1000 c.c. of normal alkali. Another definition is given by

$$\text{Equivalent} = \frac{\text{Molecular Weight}}{\text{Basicity}}$$

Purification of Liquids and Solids

The chief processes used in the purification of organic compounds are those of drying, crystallisation, sublimation, distillation, and steam distillation, and all are employed both in preparative and qualitative work.

Drying of Solids and Liquids

It is frequently necessary to remove water from solids, liquids and solutions before purification. This applies especially to

solvents such as ether after they have been used for extracting organic compounds from aqueous solutions or suspensions. Solids do not always need to be perfectly dry before purification. For example, moist compounds can be crystallised from solvents such as alcohol and acetone which are soluble in water. With solvents such as benzene and chloroform the substance must first be freed from moisture. This is done either by placing it in a desiccator and allowing it to stand over concentrated sulphuric acid or phosphorus pentoxide in vacuo for several hours, or by dissolving the substance in ether and drying the solution as outlined below. Small quantities may be dried by pressing the compound on porous plate. It sometimes happens that an apparently dry substance, on dissolving in benzene or similar solvent, gives a turbid solution due to the presence of small quantities of water. The solution is made clear by being boiled with a few grains of calcium chloride for a short time followed by filtration.

Liquids and solutions are dried by first removing, if possible, water by decantation, and then adding a dehydrating reagent. Such reagents must not react chemically with the liquid or solute. There are two types of reagent, some reacting with water to form other compounds (*e.g.*, P_2O_5), while others form hydrates (*e.g.*, $CaCl_2$). With the latter type dehydration is not complete, as there is an equilibrium between the salt and water on the one hand and the hydrate on the other. Drying is hastened by shaking and gentle warming.

The following reagents are commonly used for drying purposes.

Calcium chloride	Must not be used with alcohols, amines, or phenols, as it combines with these substances.
Potassium hydroxide	Used for amines and heterocyclic bases.
Potassium carbonate Sodium sulphate (anhydrous) . . . Magnesium sulphate (anhydrous) . .	Used with sensitive compounds which are decomposed by stronger reagents.

Sodium or magnesium sulphate is the safest reagent to use for "unknown" compounds.

The general procedure is to allow the solution or liquid to stand for several hours in contact with the dehydrating reagent, which is then removed by filtration. Since the rate of filtration is proportional to the filtering surface, it is best to use fluted filter-papers. Care must be taken not to add too much drying reagent, a few pieces of calcium chloride being usually sufficient. If, after some time, the dehydrating agent has completely disappeared and only a sludge remains, more of the agent is added.

Crystallisation

Organic substances are generally purified by crystallisation or distillation, the former method being used for compounds which melt above 40°, and the latter for compounds which are liquids at this temperature. Sometimes both methods are applied with success. The importance of crystallisation is evident since the resulting crystalline compounds have sharp melting points which serve for identification. Moreover, small quantities of substances are much more easily handled in the crystalline than in the liquid state, and for this reason liquids are often converted into solid derivatives, which are then purified by crystallisation.

Crystallisation in organic chemistry generally means the deposition of crystals from a solution of the substance either in an organic solvent or in water. It is effected by dissolving the substance in the minimum volume of a boiling solvent, filtering off any undissolved impurity, cooling the solution, and thus obtaining the compound in the crystalline state.

The following conditions are necessary for effective crystallisation.

1. The solvent must be chemically indifferent to the compound to be crystallised.

2. The compound must be readily soluble in the hot solvent, but only sparingly in the cold solvent.

3. Impurities must be either completely insoluble or completely soluble in the solvent.

The choice of solvent is extremely important and is chiefly a matter of experience, since there are few rules that can safely

be given. The rule that compounds dissolve in liquids of similar structure is useful, but has many exceptions, and must therefore be used with caution. The general procedure when dealing with an "unknown" is to try out solvents in the following order—ethyl alcohol, benzene, petrol ether, glacial acetic acid, and water. About 0·1 g. of the compound is dissolved in not more than 2 or 3 c.c. of boiling solvent. The solvent is satisfactory if it completely dissolves the compound and when cooled deposits the compound in the form of crystals. Ethyl alcohol is the solvent most commonly used; glacial acetic acid is serviceable for many high-melting compounds or for compounds which are only lightly soluble in alcohol, etc. Compounds such as the aromatic acids crystallise readily from boiling water.

Other solvents are acetone, methyl alcohol, ethyl acetate, chloroform, carbon disulphide, trichlorethylene, dioxan, tetralin, etc. High-boiling solvents such as nitrobenzene and tetralin are often used for substances which are practically insoluble in the common solvents.

If a suitable solvent cannot be found, a mixture of two solvents may prove effective. Thus mixtures of ethyl alcohol and water, benzene and petrol ether, etc., are often used. The compound is dissolved in the minimum amount of one solvent (boiling) in which it is the more soluble, and the other solvent is added until the boiling solution is turbid. The solution is left to cool, and crystals separate. It is evident that the method is applicable when the compound to be crystallised is soluble in one of the solvents and only sparingly soluble in the other. In this connection the following mixtures are commonly used—water and alcohol, glacial acetic acid and water, acetone and water, benzene and chloroform, benzene and petrol ether. A mixture of alcohol and ether is very useful for low-melting compounds. The compound is dissolved in the minimum of boiling alcohol and cooled. Ether is then added to the mixture until the oil which has separated dissolves, and the solution is allowed to stand in a crystallisation dish. The ether evaporates much more quickly than the alcohol, and after several hours a good yield of crystals is frequently obtained.

In qualitative chemistry, where only small quantities of

material are handled, crystallisations are carried out in test-tubes. Even with inflammable solvents (ether, light petroleum, and carbon disulphide excepted) there is no danger provided reasonable care is taken in heating. The substance to be crystallised is placed in a test-tube, a little solvent is added, and the mixture heated to the boiling point over a medium-sized bunsen flame, an insufficient quantity of solvent being taken so that

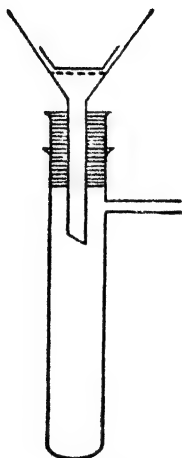
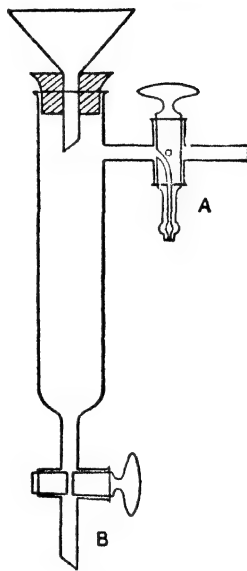



Fig. 8. Fig. 9.

all the substance does not dissolve. More solvent is then added, drop by drop, until a clear solution is obtained, or until only impurities remain. The solution is filtered while hot through a Hirsch filter (see below), and the filtrate cooled by placing the test-tube in running water. If the compound does not crystallise well, it is advisable to allow the solution to cool very gradually. The crystals are then separated by means of a Hirsch funnel with a receiver attached to a filter pump (Fig. 8). To use this apparatus the perforated base of the funnel is first covered with

a piece of filter-paper cut so as to fit accurately. The paper is then moistened with a little of the solvent, and after suction has been applied, pressed down with the finger-nail. The contents of the test-tube are poured into the filter funnel, any crystals remaining in the test-tube being washed out by means of the filtrate. After the crystalline mass has been pressed down with a spatula or small glass stopper to allow as much as possible of the mother-liquor to drain through, a specimen is removed, dried on porous plate, and its melting point determined.

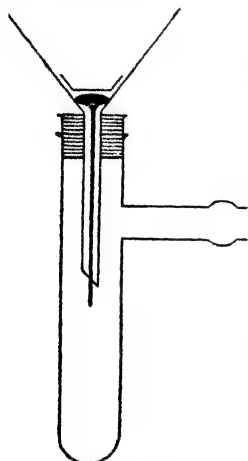



Fig. 10.

If the melting point is not satisfactory, the substance is recrystallised, a different solvent being on occasion used. Otherwise the compound is ready for further examination.

A very useful modification of the apparatus just described is the Irvine filtration apparatus (Fig. 9). By means of the three-way stop-cock (*A*) the pressure in the tube may be released, the filtrate runs out through the tap (*B*) at the bottom of the tube, and may be used for washing out any crystals which still remain in the test-tube.

For very small quantities of precipitate the Diepolder apparatus (Fig. 10) is invaluable. The funnel has a diameter of about 1 in., and the filter tube is 2—3 ins. long. In the funnel is placed a thin glass rod with a small glass plate at one end. The rod is easily made by heating a glass rod in a blow-pipe flame and drawing it out when hot. The plate is formed by heating one end of the thin rod and pressing it against a metal surface. When in use, the top of the plate is covered by a filter-paper, which is conveniently cut out by means of a cork-borer of suitable diameter. The filtration is performed in exactly the same manner as with the Hirsch apparatus.

It is sometimes difficult to induce a solution of oil to crystallise. In such cases the walls of the test-tube are scratched with the jagged end of a glass rod, or a crystal of the compound is added

and the solution stirred or shaken. *Whenever a substance is obtained in the crystalline state, a small sample is kept: even though it is very impure, it will be satisfactory for " seeding out " in later crystallisations.*

Crystallisation is often a slow process, and it may be desirable to leave the solution in a cold place overnight, or even for several days. Substances which melt below 60° C. tend to separate as oils or oily solids. This can sometimes be avoided by immersing the hot solution in a beaker of hot water, which is then left to cool to room temperature. The use of low-boiling solvents such as petrol ether (40—60°) or methyl alcohol facilitates the crystallisation of such substances: the advantages of ether-alcohol mixtures in this connection have already been mentioned (p. 16).

The last traces of solvent are removed by pressing the crystals on porous plate or by placing them on sheets of filter-paper and leaving them exposed to the air. Small samples are generally freed from solvent by pressing on porous tile. For quantitative work vacuum desiccators are used, generally with sulphuric acid or phosphorus pentoxide as drying agent. Ordinary desiccators are of little value for removing traces of solvent, but may be employed to protect compounds from the moisture of the atmosphere.

Many liquids are purified by conversion into solid derivatives, which are first crystallised and finally converted back into the original compound. Thus a number of aromatic compounds yield picrates by interaction with picric acid. These double compounds are readily purified by crystallisation from benzene, alcohol, etc., and when treated with aqueous ammonia yield the original compound free from impurity. Similarly, aldehydes can be separated from many impurities by the formation of bisulphite derivatives, which on treatment with sodium carbonate solution give the purified aldehyde. Solids which are insoluble in the common solvents may be purified by conversion into derivatives which are crystallisable. Thus certain carboxylic acids, such as terephthalic acid, are difficult to purify, but their methyl esters are readily purified by crystallisation from methyl alcohol.

Distillation. Fractional Distillation

Many liquids distil without decomposition, and may be purified in this manner. Liquids may thus be separated from non-volatile matter. In many cases, however, two or more volatile liquids have to be separated from each other. Such mixtures boil over a large range of temperature, since the composition of the mixture is continually changing owing to the more volatile component passing over more quickly. Separation cannot be effected with the ordinary distillation apparatus unless the liquids have widely different boiling points, but by using a fractionating column (Fig. 5) it is possible to achieve a more or less complete separation even when the boiling points lie relatively close together.

Fractionating columns function in the following manner. Vapour rising in the column is partially condensed, yielding vapour richer in the more volatile component and liquid richer in the less volatile component. The column is so constructed that the condensed liquid comes into intimate contact with the hot rising vapour, and partial evaporation results. Thus in the column there is a continuous series of condensations and evaporations which result in the more volatile constituent passing over into the receiving vessel and the less volatile constituent returning to the distillation flask.

A single fractional distillation is often not sufficient to separate two liquids. The mixture is separated by collecting portions or fractions every five or ten degrees and redistilling each fraction several times. An example will help to make the process clear. A mixture of 50 c.c. carbon tetrachloride and 50 c.c. toluene was distilled through an eight-bulb column, and several fractions were collected as shown in the table. Fraction *A* was then redistilled, any distillate coming over before 75° C. being discarded. When the temperature reached 80°, fraction *B* was added to the flask and distilled: in this way 19 c.c. of liquid boiling at 75—80° were collected. When the temperature reached 90° C. fraction *C* was added, and the process continued (fractions *D*, *E*, and *F* being added at suitable points) until only a residue boiling over 108° C. was left in the flask. A third

fractionating gave two samples of fairly pure carbon tetrachloride and toluene.

Fraction.	Temperature Range, ° C.	First Distillation, c.c.	Second Distillation, c.c.	Third Distillation, c.c.
A	75–80	3	19	34
B	80–90	40	27	12
C	90–100	26	12	5
D	100–105	9	5	4
E	105–108	17	26	29
F	Residue	4	4	5
Total volume of fractions		99	93	89
Total loss during distillations		1	7	11

It should be noted that since the efficiency of a distillation process is dependent on many factors, such as the nature of the fractionating column, the rate of distillation, etc., the above table gives only an indication of the process and its possibilities. Practically complete separation can often be obtained with good columns and careful manipulation.

In qualitative work much smaller quantities of material are handled than in the experiment given above, and it is not often possible to carry out more than one fractionation, even when a mixture is present. In the case of a single liquid, most of the distillate comes over at one temperature, whilst with a mixture two main fractions are obtained at approximately the boiling points of the constituents. It is sometimes advisable to heat the flask in an oil or metal bath. Oil baths may be heated to about 270°, while higher temperatures may be obtained with metal baths, the metal consisting of a mixture of 2 parts bismuth, 1 part lead, and 1 part tin. Better fractionation is obtained by the use of such baths than by heating with a bunsen flame, as superheating is thereby largely avoided.

Distillation under Reduced Pressure

In cases where distillation at atmospheric pressure is accompanied by decomposition, purification can be effected by distillation under reduced pressure. Under a pressure of 10

—20 mm., a pressure easily obtainable by means of the water-pump, the boiling point of a liquid is lowered approximately a hundred degrees. The apparatus is shown in Fig. 11. A small Claisen flask, fitted with rubber stoppers, is attached to a Gooch filter-tube which acts as receiver. To prevent bumping a very fine capillary is inserted in one of the stoppers so that the end of the capillary reaches almost to the bottom of the flask. On suction being applied a continuous stream of small bubbles is drawn through the liquid in the flask. The capillary should be

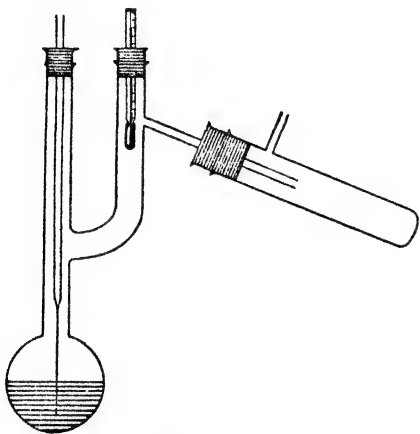
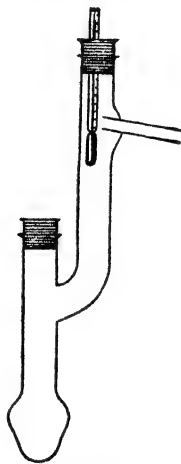



Fig. 11. Fig. 12.

a fine thread, so that on blowing through with the end under ether a slow succession of small bubbles is produced. The receiver is connected through a manometer to a water-pump and is cooled by a stream of running water. Leaks in the apparatus must, of course, be avoided if a good vacuum is to be obtained, and for this reason rubber stoppers are used instead of corks. The distillation is performed in the same manner as with an ordinary distillation.

The apparatus shown in Fig. 12 is recommended for the distillation of small quantities of liquid: 0·5—1 g. The trap at the outlet to prevent impurities from the stopper passing into the distillate should be noted.

In recording distillation results it is essential to state the pressure as well as the temperature at which the liquid distils. Thus b.p. 230°/11 mm. means that the liquid boils at 230° under a pressure of 11 mm.

Steam Distillation

A mixture of two immiscible liquids, on being heated, behaves quite differently from a homogeneous mixture, which can usually be separated by fractional distillation. Each component exerts its own vapour pressure independently of the other, and the mixture finally distils when the sum of the vapour pressures equals that of the atmosphere, the temperature of distillation being lower than that of either of the constituents. Consequently many liquids, such as aniline (b.p. 184°), can be distilled when heated with water, or, better, when steam is passed through them, the distillate consisting of a mixture of water and the organic compound. This method is very useful in separating certain mixtures (see Chapter VI), and also for separating compounds from "tar," which is often produced in reactions such as the Friedel–Craft reaction.

The method is exactly the same as that employed for preparative work, except that it is conducted on a smaller scale.

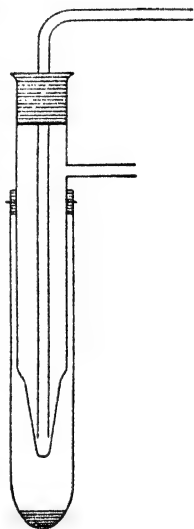



Fig. 13.

Sublimation

Only a limited number of compounds can be purified by sublimation, but certain compounds, such as naphthalene and anthraquinone, are frequently purified by this method. Indeed, small quantities of quinones are best purified in this way. For small quantities of substance the apparatus shown in Fig. 13 is suitable. Water passes through the inner tube, which acts as a condenser, and the outer tube, containing the compound to be purified, is gently heated by a micro-flame. The sublimate collects on the bottom of the condenser.

An interesting discussion by Kempf on the use of sublimation in organic chemistry is found in the *Journal für praktische Chemie*, 1908, **78**, 201.

Decolorisation

Compounds containing small amounts of "tar" or colouring matter may be purified by **adsorption**. The purification is best effected by boiling the substance in solution with animal charcoal, which adsorbs the impurities. The efficiency of the process depends partly on the grade of charcoal used and partly on the solvent, water being better than alcohol, and the latter better than benzene.

The substance is completely dissolved in boiling solvent, and about $\frac{1}{30}$ of its weight of animal charcoal is added *very carefully*, otherwise the solution may froth over. The solution is then boiled for five or ten minutes (in the case of benzene solutions an hour may be necessary), and is then filtered hot through a Hirsch funnel. Several filtrations are sometimes necessary to remove the last traces of charcoal. The clarified solution deposits crystals on cooling, or, if necessary, is evaporated down to give the purified compound.

Chromatographic Adsorption

This method (see also Chapter VI) is used for removing small quantities of impurities when other methods are either useless or extremely tedious. The student is referred to the excellent monograph on the subject by Zechmeister and Cholnoky.

References

Meyer, Hans, *Analyse und Konstitutionsermittlung organischer Verbindungen.*
Gattermann, *Laboratory Methods of Organic Chemistry.*
Bernhauer, *Einführung in die organisch-chemische Laboratoriumstechnik.*
Findlay, *Practical Physical Chemistry.*
Kofler and Kofler, *Mikroskopische Methoden in der Mikrochemie.*
Morton, *Laboratory Technique in Organic Chemistry.*
Hartshorne and Stuart, *Crystals and the Polarising Microscope.*
Zechmeister and Cholnoky, *Die Chromatographische Adsorptionsmethode.*

CHAPTER II

IDENTIFICATION OF ORGANIC COMPOUNDS. GENERAL PROCEDURE. PRELIMINARY TESTS

General Procedure

THERE are three stages in the identification of organic compounds :—

1. Preliminary tests.
2. Supplementary tests.
3. Preparation of crystalline derivatives, and examination of their physical properties.

The purified compound is first subjected to the preliminary tests outlined in this chapter. Until the student has gained some experience, *all* the preliminary tests should be systematically performed. After some practice clues or guesses may be followed up, and specific tests applied. *The correctness of such guesses must be carefully tested experimentally.* For example, if a liquid is thought to be aniline (odour and colour), the following tests must be carried out : boiling point determination, ignition test, solubility in hydrochloric acid, diazotisation test, Runge's test, and the preparation of acetyl and benzoyl derivatives. Short cuts are often dangerous, and it is advisable in most cases to follow the systematic procedure given in this chapter. These preliminary tests classify compounds according to their chemical reactions. Thus aniline will be found to be an aromatic amine, acetic acid an aliphatic carboxylic acid, etc.

The supplementary tests lead to the identification of the compound. For instance, a compound found by the preliminary tests to be a carbonyl derivative, is shown to be an aldehyde if it gives a positive test with Schiff's reagent. The compound is then identified by its melting point or boiling point. Specific

tests may be applied for certain compounds, *e.g.*, aniline gives a violet coloration with bleaching solution (Runge's test). Colour tests are sometimes useful, ferric chloride, for example, giving colorations with many phenols. Colour tests must, however, be applied with great care, as they are often extremely sensitive. Thus *p*-hydroxybenzoic acid in the pure state gives a yellow colour with ferric chloride, but the ordinary acid sometimes gives a violet colour owing to the presence of traces of salicylic acid. Negative colour tests are decisive. Positive colour tests generally serve only as indications, and not as conclusive tests.

The supplementary tests are given in Chapter III, and colour tests in Chapters II and III.

The preparation of crystalline derivatives is the final stage in the identification of compounds. The derivatives are purified, their physical properties, especially their melting points, are determined, and compared with those quoted in Section B. Thus an aromatic amine giving an acetyl compound, m.p. 114°, and a benzoyl derivative, m.p. 163°, is shown beyond all doubt to be aniline. In this way compounds are identified with certainty.

It must be emphasised that many of the qualitative tests are subject to certain limitations. A substance responding to the diazo test is generally assumed to be an aromatic amine, but some compounds, such as formanilide, are readily hydrolysed, and consequently yield diazonium solutions with sodium nitrite and hydrochloric acid.

Most of the tests given in this book can be carried out with 0·1 g. or less, and even in the preparation of derivatives 0·5 g. or less is sufficient. The student should acquire the habit of using small quantities of material so that he can identify compounds when given only one or two grammes of a compound. Frequently in research considerably smaller quantities are available for identification and analysis.

Chapter IV is intended as a help in understanding the tests employed and in choosing suitable tests and derivatives. Part B gives data relating to a number of important organic compounds.

Preliminary Tests

1. Physical Properties

The most important properties—melting point, boiling point, and density—have already been discussed (Chapter I). A compound boiling at a temperature lower than 80° must be aliphatic.

Odour. Some of the common types of compounds with characteristic odours are: esters, phenols, aliphatic amines, aromatic amines, mercaptans, *iso*cyanides. Benzaldehyde, nitrobenzene, and benzonitrile all have the odour of bitter-almond oil.

Colour. Certain classes of compound are often coloured, *e.g.*, nitro-compounds such as the nitranilines. Other types are invariably coloured, *e.g.*, quinones, azo-compounds, etc. The colour of some compounds, however, is due to impurities. Aniline, for example, when pure is colourless, but generally has a brown colour. It is easy after a little experience to distinguish between true and acquired colour.

Appearance. Compounds such as the osazones have a characteristic appearance under the microscope. The fact that a compound is crystalline is often of service. Thus ammonium oxalate is similar in many of its reactions to oxamide, but its crystalline structure is in marked contrast to the powder form in which oxamide is usually obtained. (See also p. 4.)

2. Ignition Test

A small quantity of the compound is gently heated on a small piece of platinum foil—about 2 cm. square is a suitable size—over a small flame. Any gas evolved is tested for ammonia by means of moist litmus paper. Substances such as urea give off ammonia on heating. The nature of the flame is also observed. Aromatic compounds burn with a smoky flame, while the aliphatic compounds burn with a non-smoky flame. It should be noted, however, that aliphatic substances with more than four carbon atoms in the molecule and compounds containing chlorine also burn with a smoky flame. Certain compounds burn characteristically. Thus urethane gives off ethyl alcohol, which

continues to burn when the compound is removed from the flame. Sugars give a "burnt sugar" smell. A white residue left on the foil after ignition indicates the presence of a metal.

3. Elements Test

Lassaigne Sodium Test.

A hard-glass test-tube, 4 ins. in length, is clamped in a vertical position, and a piece of *clean* sodium about the size of a small pea is placed in it. The tube is heated by a small bunsen flame until the sodium melts and a layer of sodium vapour is formed above it. A little of the compound—10—20 mg.—is dropped into the tube, which is then heated more strongly, the flame being removed at intervals to allow any liquid which may have condensed on the sides of the tube to fall back on to the sodium. The tube is finally heated to a red heat, and is then immersed in 15 c.c. of water in a porcelain basin, the safety of the student being insured by a piece of wire-gauze held immediately above the basin. When the bulb has cracked and all the unused sodium has dissolved in the water, the solution is filtered, and divided into four portions.

Portion 1.

A few drops of freshly prepared ferrous sulphate solution are added. A black precipitate is formed if the original compound contains **sulphur.** The suspension is acidified with a few drops of concentrated hydrochloric acid. A blue precipitate indicates the presence of **nitrogen.** If only a blue or greenish-blue solution is obtained, the solution is filtered, a blue precipitate then becoming visible on the filter paper. When sulphur is present it is advisable to add a few drops of ferric chloride solution along with the ferrous sulphate.

Portion 2.

The presence of **sulphur** is also shown by adding lead acetate solution (made by mixing three drops of lead acetate solution with 2 c.c. of 10% sodium hydroxide solution) when a black precipitate is obtained. If only a brown solution is obtained

it is filtered, and the filter paper examined. A brown deposit indicates sulphur.

Portion 3.

The solution is acidified with nitric acid, and silver nitrate solution is added. A precipitate denotes the presence of halogen. A white precipitate shows **chlorine,** whilst a yellow precipitate shows **bromine** or **iodine.**

If nitrogen or sulphur is present in the compound, the solution must first be *boiled* with 5 c.c. of dilute nitric acid (1 part by volume of concentrated nitric acid and 2 parts of water) for 5 minutes before adding the silver nitrate. This is to destroy any cyanide or sulphide which interferes with the test.

Portion 4.

If halogen has been detected, the solution is acidified with dilute sulphuric acid, and chloroform (2 c.c.) is added. A drop of *freshly prepared* chlorine water is added, and the mixture is shaken. The colour of the chloroform layer indicates the nature of the halogen.

Colourless	Chlorine.
Brown	Bromine.
Violet	Iodine.

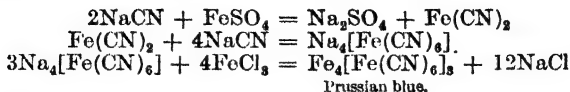
Should iodine be shown to be present, more chlorine water is added. If a brown colour persists in the chloroform layer bromine is also present.

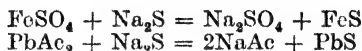
Miceli (*J. Chem. Educ.*, 1936, **13**, 515) has recently introduced another method for the sodium ignition. The method works well, and is especially valuable for volatile compounds.

Middleton (*Analyst*, 1935, **60**, 154) dispenses with the use of sodium, and uses instead sodium carbonate—sugar or sodium carbonate–zinc-dust mixtures. The method works extremely well, and has certain advantages over the sodium method.

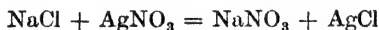
The Lassaigne sodium test depends on the formation of sodium cyanide, sodium sulphide, and sodium halide. The cyanide ion is detected by the addition of ferrous sulphate (which usually

contains a little ferric salt) and hydrochloric acid. A precipitate of Prussian blue is formed :

$$2NaCN + FeSO_4 = Na_2SO_4 + Fe(CN)_2$$
$$Fe(CN)_2 + 4NaCN = Na_4[Fe(CN)_6]$$
$$3Na_4[Fe(CN)_6] + 4FeCl_3 = \underset{\text{Prussian blue.}}{Fe_4[Fe(CN)_6]_3} + 12NaCl$$

The sulphide ion gives a black precipitate with ferrous sulphate or lead acetate :

$$FeSO_4 + Na_2S = Na_2SO_4 + FeS$$
$$PbAc_2 + Na_2S = 2NaAc + PbS$$

The presence of sodium sulphide sometimes reduces all the ferric salt necessary for the nitrogen test. It is therefore advisable to add a little ferric chloride solution when testing for nitrogen.

The halide ion gives a precipitate of the silver halide.

$$NaCl + AgNO_3 = NaNO_3 + AgCl$$

Beilstein Halogen Test.

The end of a copper wire is fixed in a cork, which acts as holder, and the other end is heated in a bunsen flame until it no longer imparts a green tinge to the flame. When cold, the wire is dipped in the substance to be tested, and heated in the edge of the flame. The compound first burns in the usual manner, and then, if it contains halogen, gives a green coloration. The test is extremely sensitive. A few substances, such as urea, thiourea, some pyridine derivatives, etc., which do not contain halogen, also give the coloration. The test is due to the volatility of the cuprous halides, and, in certain instances, of cuprous cyanide.

4. Solubility

The solubility of the compound in water, 10% sodium hydroxide, and dilute hydrochloric acid is determined, 0·2 c.c. or 0·2 g. of the compound being placed in a test-tube and shaken in the cold with 3 c.c. of the solvent. The compound is said to be soluble when it completely dissolves in this amount of solvent.

Certain deductions can be made from solubility determinations, but great care must be exercised, as our knowledge of the relationship between chemical constitution and physical proper-

ties (in this case solubility) is imperfect. The following lists may, however, be helpful.

Soluble in Water.

Polyhydroxy compounds . *e.g.*	Carbohydrates. Pyrogallol. Glycerol.
Lower alcohols . . .	Ethyl alcohol.
Lower aldehydes . . .	Acetaldehyde.
Lower ketones . . .	Acetone.
Aliphatic amines . . .	Ethylamine.
Aliphatic amino acids . .	Glycine.
Lower carboxylic acids . .	Acetic acid.
Sulphonic acids . . .	Benzenesulphonic acid.
Salts	Aniline hydrochloride. Sodium benzoate.

Soluble in Sodium Hydroxide Solution.

Acids	Benzoic acid.
Phenols	Phenol.
Oximes	Benzil oximes.

Soluble in Hydrochloric Acid.

Amines	Aniline.
Hydrazines	Phenylhydrazine.
Heterocyclic compounds . .	Quinoline.

It is, of course, obvious that if a compound is soluble in water, its solubility in alkali or acid gives little further information. Thus, since pyridine dissolves in water, its solubility in dilute acid gives no clue to its basic nature. On the other hand, quinoline, which does not dissolve in water, is at once shown to be a base by its solubility in acid. The reaction to litmus of substances soluble in water should be noted. Acid reaction: carboxylic and sulphonic acids. Alkaline reaction: amines such as methylamine.

For detailed descriptions of the determination of structure by solubility tests the books by Kamm and by Shriner and Fuson given in the bibliography at the end of the book should be consulted.

5. Sodium Hydroxide Test

About 0·2 g. of the compound is dissolved or suspended in 2 c.c. of water, 10% caustic soda solution (2 c.c.) is added, and the mixture shaken.

Acids, phenols, and oximes dissolve instantly. Acid chlorides such as benzoyl chloride, and acid anhydrides dissolve on warming and shaking the mixture.

Quinones and polyhydric phenols give a black coloration. Carbohydrates and monohydric phenols give a coloration or darken on gentle heating. In some cases the solution must be allowed to stand for a few minutes after heating.

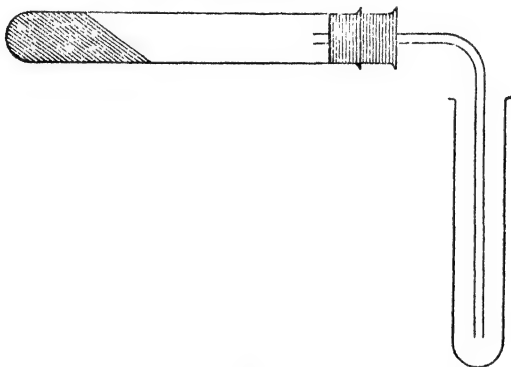



FIG. 14.

Salts such as aniline hydrochloride yield an oily suspension of the free base; chloral gives chloroform.

Ammonia (detected by moist litmus paper) is given off from different types of compounds : from ammonium salts in the cold; by warming amides, imides, and urethanes; and by boiling cyanides for several minutes.

6. Soda-Lime Test

A mixture of the compound (0·5 g.) and soda-lime (2 g.) is well ground in a mortar, and is then placed in a hard-glass test-tube. Another gramme of soda-lime is added, a cork with an outlet tube is inserted (Fig. 14), and the tube is then strongly heated.

Ammonia is given off by many compounds, as in the case of the sodium hydroxide test, and by other compounds such as uric acid. Amines, easily recognised by their fish-like odour, are obtained from amino acids such as glycine. Substituted amines (*e.g.*, benzanilide) yield the free amine, generally as an oil which is collected in the receiving tube and examined.

Carboxylic acids give hydrocarbons. Benzoic acid, for instance, gives benzene which can be collected and identified.

7. **Sulphuric Acid Test**

About 0·2 g. of the substance is shaken with 2 c.c. cold concentrated sulphuric acid. Only saturated and aromatic hydrocarbons are insoluble. Many compounds give characteristic colorations (see p. 44).

Uric acid dissolves on gentle heating, but is precipitated unchanged on dilution with water.

Gases are given off by some acids when heated. Carbon monoxide, which burns with a characteristic blue flame at the mouth of the test-tube, is given off by formic, lactic, and malic acids, and less readily by benzilic, diphenylacetic, mandelic, and glycollic acids.

Oxalic acid gives carbon dioxide and carbon monoxide. The carbon dioxide must be tested for first by leading the gases into lime-water.

Carbonates and carbonic acid derivatives yield carbon dioxide.

Salts and derivatives of these acids also respond to the test. Thus urea gives off carbon dioxide, showing it to be a derivative of carbonic acid.

In these tests the sulphuric acid removes the elements of water, *e.g.*, $H{\cdot}COOH = CO + H_2O$.

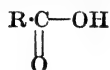
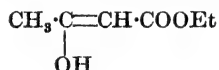
8. **Ferric Chloride Test**

A little of the compound is shaken with 10 c.c. water, and two or three drops of neutral $FeCl_3$ solution (see Appendix) are added. Alcohol is sometimes used instead of water.

Phenolic compounds give characteristic colours, as do many enolic compounds. A few amines, such as *p*-phenetidine, *o*-phenylenediamine, etc., give colours with acid ferric chloride.

Aromatic acids of the benzoic acid type, as well as hippuric, cinnamic, and phenylacetic acids, give buff-coloured precipitates. Neutral solutions are employed. These are made by dissolving the acid in a slight excess of very dilute ammonia, and boiling until the solution is neutral to litmus.

Some aliphatic acids also give colours with ferric chloride. Hydroxy acids such as tartaric, malic, and citric acids give distinct yellow colorations. Formates and acetates give reddish-brown colorations, and the salts of succinic acid yield a reddish-brown precipitate.

It will be seen that ferric chloride gives colorations or precipitates with compounds containing the C—OH grouping.

9. Dinitrophenylhydrazine Test

The stock solution of 2 : 4-dinitrophenylhydrazine (see Appendix) is well shaken, and 5 c.c. are added to 5 c.c. ethyl alcohol. A few drops of the carbonyl compound are added, and the mixture is heated to the boiling point. Two drops of concentrated hydrochloric acid are then added, and the solution is boiled for 30 seconds. Should no precipitate separate on cooling, water is added until crystals appear. The dinitrophenylhydrazones are crystallised from alcohol, or, in the case of the higher-melting hydrazones, from glacial acetic acid or tetralin.

The reagent reacts immediately with most carbonyl compounds to give crystalline derivatives, and is the best reagent for the detection and identification of aldehydes and ketones.

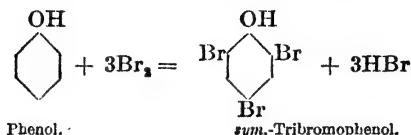
10. Bromine Test

The substance to be tested is dissolved in glacial acetic acid or carbon tetrachloride, and a solution of bromine in the same solvent is added until the colour of bromine persists. The solution on standing for 15 minutes or longer deposits crystals of the bromo-compound. If crystals are not obtained, water is added or the solvent is removed by evaporation until a precipitate is obtained. The bromo-compounds are purified by washing

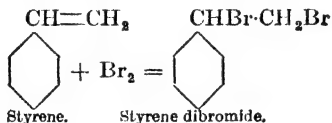
with sodium bicarbonate solution followed by crystallisation from alcohol (cf. p. 82).

Aromatic amines, aromatic ethers, and phenols react with bromine without the aid of a catalyst, hydrobromic acid being evolved.

$$C_6H_5OH + 3Br_2 = C_6H_2Br_3OH + 3HBr$$

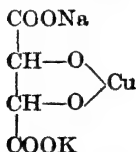
Phenol. *sym.*-Tribromophenol.

Unsaturated compounds react, but no hydrobromic acid is formed.

$$C_6H_5CH{=}CH_2 + Br_2 = C_6H_5CHBr{\cdot}CH_2Br$$

Styrene. Styrene dibromide.

11. Fehling's Solution Test

About 0·2 g. of the compound is heated with 5 c.c. Fehling's solution (see Appendix) to the boiling point. Reducing sugars, aliphatic aldehydes, and hydrazines produce a red precipitate of cuprous oxide.

Cupric salts are reduced in alkaline solution, but in the presence of alkali the cupric ions are precipitated as cupric hydroxide, and are not readily available for reduction. To overcome this difficulty sodium potassium tartrate is added, which prevents the precipitation of the hydroxide by forming a complex with the cupric ions, possibly with the following structure—

$$\begin{array}{l} COONa \\ | \\ CH{-}O\diagdown \\ | \qquad\quad\; Cu \\ CH{-}O\diagup \\ | \\ COOK \end{array}$$

12. Phosphorus Pentachloride Test

A small quantity of phosphorus pentachloride is placed in a test-tube, and a few drops of the carefully dried compound are added. A brisk or violent evolution of hydrochloric acid is evidence that the compound is an acid or an alcohol. The

method is useful for distinguishing between alcohols and ethers as the latter are inactive towards phosphorus pentachloride.

$$ROH + PCl_5 = RCl + HCl + POCl_3$$

13. Picric Acid Test (cf. p. 84)

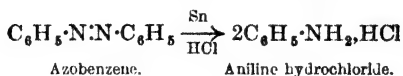
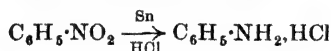
The compound is dissolved in the *minimum quantity* of ethyl alcohol, and the solution added to a boiling saturated solution of picric acid. The picrate which separates on cooling is crystallised from alcohol, and its melting point determined.

These picrates are either molecular compounds or salts of bases, and are formed by aromatic hydrocarbons, amines, amino acids, hydrazines, and alkaloids. Benzene and some of the other simpler aromatic hydrocarbons form picrates which are so unstable that it is impossible to isolate them under ordinary conditions.

14. Tin and Hydrochloric Acid Test

Two or three drops of the compound (or the corresponding amount of solid) are added to concentrated hydrochloric acid (3 c.c.). A piece of tin is then added, and the mixture is gently heated. If a clear solution is obtained, the compound is a nitro, nitroso, hydrazo, azoxy, or azo compound. These compounds are reduced to amines which dissolve in the hydrochloric acid. Sometimes a double salt of the amine and stannic chloride separates out as a white, crystalline mass.

$$C_6H_5 \cdot NO_2 \xrightarrow[HCl]{Sn} C_6H_5 \cdot NH_2,HCl$$

$$\underset{\text{Azobenzene.}}{C_6H_5 \cdot N{:}N \cdot C_6H_5} \xrightarrow[HCl]{Sn} \underset{\text{Aniline hydrochloride.}}{2C_6H_5 \cdot NH_2,HCl}$$

The test, of course, is not applicable to compounds, such as the amines, which are soluble in hydrochloric acid.

Compounds responding to this test may often be further classified by their colour.

Nitro-compounds .	Frequently yellow or orange.
C-Nitroso-compounds .	Colourless. Green when fused or in solution.
Hydrazo-compounds .	Colourless turning red in air.
Azoxy-compounds .	Pale yellow.
Azo-compounds . .	Invariably red or orange in colour.

15. Alcoholic Potassium Hydroxide Test

This test is applied to compounds containing halogen in cases where it is important to determine whether or not the halogen is mobile, *i.e.*, is easily removed from the compound. The compound (0·2 g.) is heated with 5% alcoholic potassium hydroxide. A precipitate of potassium chloride or bromide is obtained from aliphatic compounds and aromatic compounds with halogen in the side-chain. The corresponding iodo-compounds do not give a precipitate, as potassium iodide is soluble in alcohol. In this case the alcoholic solution is acidified with dilute nitric acid, and silver nitrate is then added. A yellow precipitate of silver iodide denotes the presence of mobile iodine.

CHAPTER III

IDENTIFICATION OF ORGANIC COMPOUNDS. SUPPLEMENTARY TESTS. COLOUR TESTS

THE preliminary tests given in the previous chapter classify the compound under examination, and further confirmatory tests are often desirable. Some of these are given in this chapter. Occasionally such tests are purely confirmatory, Molisch's test, for example, being employed when a compound is thought to be a carbohydrate. In other cases the supplementary tests classify a compound more exactly. For instance, Hinsberg's test shows whether an amine is primary, secondary, or tertiary.

The colour reactions given may also be regarded as supplementary tests.

Tests

(Numbers in column 3 refer to the number of the test in this chapter)

Nature of Compound.	Test.	No.
Containing $CH_3 \cdot CO$ group	Iodoform formation	1
Reducing compounds	Tollen's reagent	2
Nitro-compounds, etc.	Phenylhydroxylamine formation	3
Phenols Nitroso-compounds	Liebermann reaction	4
Phenols	Phthalein formation	5
Aldehydes	Schiff's reagent	6
Carbohydrates	Molisch's reagent	7
Carbohydrates	Barfoed's reagent	8
Pentoses	Orcinol reagent	9
Pentoses	Phloroglucinol reagent	10
Nitrites	Phenylindole test	11
Primary aromatic amines	Diazotisation test	12
Primary amines	Carbylamine formation	13
prim.-, *sec.*-, and *tert.*-Amines	Hinsberg's test	14
α-Amino acids	Ninhydrin test	15
Anilides	Tafel's reagent	16
Urea, etc.	Biuret formation	17
Proteins and phenols	Millon's reagent	18
Unsaturated compounds	Baeyer's reagent	19

1. Iodoform Reaction

Five drops of the compound (or an equivalent weight of solid) are added to 10% sodium hydroxide (3 c.c.). A concentrated solution of iodine in potassium iodide is then added drop by drop until a faint yellow colour persists. If no precipitate is formed the solution is heated to boiling. The solution on cooling deposits a yellow precipitate of iodoform, which is identified by its odour and melting point.

Dioxan is recommended as a solvent for those compounds which are not soluble in water (*J. Amer. Chem. Soc.*, 1934, **56**, 1638).

The iodoform test is given by compounds such as ethyl alcohol which are easily oxidised to compounds containing the $CH_3 \cdot CO$ group or by compounds containing this group.

2. Tollen's Reagent. Ammoniacal Silver Nitrate

Equal volumes of 10% silver nitrate and 10% sodium hydroxide are mixed, and concentrated ammonia is added drop by drop until the silver oxide formed just dissolves. A small quantity of the compound to be tested is shaken *in the cold* with this solution. A black precipitate of silver is formed, but if precautions are taken, a bright mirror can be obtained.

On long standing Tollen's reagent forms a very explosive precipitate, and for this reason it should be prepared immediately before use.

The reagent is used in testing for aldehydes, reducing sugars, quinones, and formic acid.

3. Reduction of Nitro-compounds, etc., to Hydroxylamine Derivatives

A small quantity of the compound is mixed with water (2 c.c.) and alcohol (2 c.c.). A few drops of calcium chloride solution and a pinch of zinc dust are added, and the solution is heated to boiling for 20 seconds. The solution is filtered, and the filtrate is found to reduce an ammoniacal solution of silver nitrate. This test is given by nitro, nitroso, azoxy, hydrazo, and azo compounds.

4. Liebermann's Nitroso Reaction

A little phenol is dissolved in concentrated sulphuric acid (1 c.c.), a crystal of sodium nitrite is added, and the solution is shaken and warmed slightly. A blue colour is obtained, which changes to red when the solution is poured into water.

This test is frequently used to detect nitroso-compounds, the sodium nitrite in the above test being substituted by a nitroso-compound. A positive reaction is obtained with nitrosamines and with many *C*-nitroso-compounds.

5. Phthalein Test

The phenol (0·2 g.) and phthalic anhydride (0·5 g.) are heated gently for 30 seconds with a small piece of zinc chloride. The melt is then cooled, and 10% caustic soda solution added. With many phenols characteristic colours are obtained.

Compound.	Colour.
Phenol	Red.
o-Cresol	Red.
m-Cresol	Blue.
p-Cresol	Nil.
Catechol	Blue.
Resorcinol . . .	Fluorescent green solution.

6. Schiff's Reagent

Two drops of the aldehyde are added to Schiff's reagent (see Appendix) *in the cold.* A magenta colour is obtained. The test must be performed in the cold, as mere heating is sufficient to restore the colour of the reagent. Aromatic aldehydes react more slowly than the aliphatic aldehydes.

The test is so sensitive that traces of aldehyde are sufficient to restore the colour.

7. Molisch's Reaction

A small amount of the compound is dissolved in water, and two or three drops of an alcoholic solution of α-naphthol are added. Concentrated sulphuric acid is then carefully poured

down the side of the test-tube. A violet colour is formed at the junction of the two layers. The test is used for detecting carbohydrates and glycosides.

8. Barfoed's Reagent

About 1 c.c. of the reagent (see Appendix) and 1 c.c. of the sugar solution are heated together in a beaker of boiling water. Monosaccharides produce a red precipitate within 2 minutes.

9. Bial's Orcinol Reaction

About 5 c.c. of the reagent (see Appendix) and a small amount of the sugar are mixed and boiled. The solution assumes first a green and finally a violet colour if a pentose is present.

10. Tollens' Phloroglucinol Reaction

A few milligrammes of the sugar are dissolved in 2 c.c. water and 2 c.c. concentrated hydrochloric acid. A small quantity of phloroglucinol is added and the solution boiled. A red colour is obtained if the sugar is a pentose.

11. Phenylindole Test for Nitrites

2-Phenylindole (0·2 g.) is dissolved in boiling alcohol, and the nitrite (0·2 g.) is added. The solution on cooling deposits 3-*iso*-nitroso-2-phenylindole, which on crystallisation from amyl acetate is obtained in the form of yellow needles, m.p. 280°. This is a simple method for detecting alkyl nitrites.

12. Diazotisation Test

Two drops or 0·1 g. of the amine are added to water (1 c.c.) containing five drops of concentrated sulphuric acid. The solution is cooled in ice, and 10% sodium nitrite solution (1 c.c.) is added drop by drop, the solution being frequently shaken. The clear solution is poured into 10% caustic soda (2 c.c.) containing 0·2 g. β-naphthol. A red precipitate is obtained if the compound is a primary aromatic amine, and after crystallisation from alcohol may be used as a derivative for identification.

13. Carbylamine Reaction

Two drops (or 0·1 g.) of the amine, two drops of chloroform, and alcoholic caustic potash (1 c.c.) are mixed and warmed. An intolerable odour of an *iso*cyanide indicates the presence of a primary amine.

14. Hinsberg's Reaction

The amine (0·5 g.), *p*-toluenesulphonyl chloride (0·5 g.), and 10 c.c. 10% caustic soda solution are heated together and shaken for 3 minutes. The solution should still be alkaline: if not, more caustic soda solution is added. If the amine is primary, a clear solution is obtained, which on acidification yields a precipitate of the sulphonyl derivative. This may be crystallised from aqueous alcohol (50%), and used as a derivative. If a secondary amine has been used, the sulphonyl derivative is insoluble in alkaline solution, and may be crystallised as above. Tertiary amines do not form sulphonyl derivatives.

Hinsberg's method must be used with care. Thus for amines with more than seven carbon atoms in the molecule a special method must be adopted, owing to the sparing solubility of the sodium salt of the sulphonyl derivatives. Another drawback is the formation of disulphonyl derivatives of primary amines. Many primary amines consequently give a mixture of sulphonyl derivatives—one being soluble in alkali, and the other insoluble. When this occurs, the mixture of solids is hydrolysed for 15 minutes with alcoholic sodium hydroxide. The solution is then diluted with water, and the monosulphonyl derivative precipitated with hydrochloric acid. It is purified from 50% aqueous alcohol.

15. Ninhydrin Test

An aqueous solution of the compound is heated in a test-tube with a few drops of a solution of ninhydrin (0·1 g.) in water (40 c.c.). A blue colour is obtained if an α-amino acid is present.

16. Tafel's Test

The compound is shaken with concentrated sulphuric acid (4 c.c.) and a small crystal of potassium dichromate is added. Many anilides and toluidides give characteristic colours.

17. Biuret Reaction

A small amount of the compound is added to 10% sodium hydroxide (3 c.c.). A dilute solution of cupric sulphate, obtained by diluting bench cupric sulphate solution until the blue colour just remains, is added drop by drop, and the solution is shaken. As the copper sulphate is added, the solution becomes first pink, then violet, and finally deep blue.

18. Millon's Test

A small amount of the compound is added to 1 c.c. of Millon's reagent (see Appendix) and the solution is gently heated if necessary. A red colour is obtained with proteins, tyrosine, and many phenols.

19. Baeyer's Test

The compound (0·1 g.) is dissolved in alcohol, and two drops of 1% potassium permanganate solution are added. The rapid appearance of a brown colour or precipitate indicates the presence of a double bond. The test is given by other compounds such as aldehydes, but in such cases decolorisation takes place much more slowly.

Colour Tests

Colour tests are used to detect certain classes of compounds, and are of special value when only small quantities of material are available. Phenols may, for example, be readily detected by the use of ferric chloride, colorations being obtained with very dilute solutions. Such tests must be used with caution, as colorations may be caused by traces of impurities. Colour tests are decisive in proving the absence of compounds, and are useful as indications of the presence of compounds, but they should not be employed for the purpose of conclusive identification. Thus a solution giving no colour with ferric chloride contains no phenol: if it gives a colour a phenol is present, but whether as the main constituent or as an impurity it is impossible to say without further tests. This in no way invalidates the use of colour tests provided their limitations are recognised.

Some colour tests have already been given, and others which are often useful are given below.

Sulphuric Acid

Many compounds of different types give brilliant colours with concentrated sulphuric acid either in the cold or on gentle warming. Some of the more important examples are given below.

Compound.	Colour.
Indene	Polymerises—red.
α-Pinene	Red.
Fluorene	Blue on heating for 2 min.
Fluoranthene	Greenish-blue.
Anthracene	Green on heating.
Triphenylcarbinol	Bright yellow.
Saligenin	Red.
Thymol	Red on warming.
Phenolphthalein	Red.
Isoeugenol	Red.
Benzhydrol	Orange-red.
Phloroglucinol	Yellowish-green ⟶ blue ppt.
Pyrogallol	Pale violet.
α-Nitronaphthalene	Blood-red.
Many glucosides	Bright colours.
Alizarin	Deep red.
Piperonal	Yellow.
Benzalacetone	Orange-red.
Benzalacetophenone	Deep yellow.
Fluorenone	Reddish-violet.
Benzanthrone	Red, green fluorescence.
Phenanthraquinone	Dark green.
Chrysoquinone	Bluish-violet.
Benzilic acid	Red.
Naphthalic acid	Violet fluorescence.
Gallic acid	Purple on heating.
Cinnamic acid	Green⟶reddish-brown on heating
Azo-compounds	Yellow or red.
Tyrosine	Red on heating.
Diphenylnitrosamine	Blue.
Carbazole	Yellow.

Benzal Chloride Test for Hydrocarbons

Certain aromatic hydrocarbons when suspended in concentrated sulphuric acid and treated with a few drops of benzal chloride give characteristic colorations on shaking (Lippmann and Pollak, *Monatsh.*, 1902, 23, 670).

Hydrocarbon.	Colour.
Anthracene	Green.
Naphthalene	Magenta.
Phenanthrene	Red.
Acenaphthene	Blue.
Fluoranthene	Carmine.
Chrysene	Yellow ⟶ green.
Pyrene	Emerald-green ⟶ blue.
Retene	Brown.
Triphenylmethane	Yellow.
Dibenzyl	Yellow.
Stilbene	Green.
Fluorene	Crimson-lake ⟶ violet.

Nitro-compounds

Many dinitro- and trinitro-compounds give colorations with acetone and caustic soda, and this test has been systematically investigated by Bost and Nicholson (*Ind. Eng. Chem.* (*Anal.*), 1935, 7, 190).

The nitro-compound (0·1 g.) is dissolved in acetone (10 c.c.) and 5% sodium hydroxide solution (3 c.c.) is added with shaking. Mononitro-compounds give no colour; dinitro-compounds give a purplish-blue colour; and trinitro-compounds give a blood-red colour. Certain exceptions have been found.

Mononitro-compounds. No colour

Dinitro-compounds

Compound.	Colour.
m-Dinitrobenzene	Purplish-blue.
1-Chloro-2 : 4-dinitrobenzene	Purplish-blue.
3 : 5-Dinitrobenzoic acid	Purplish-blue.
2 : 4-Dinitroanisole	Purplish-blue.
2 : 4-Dinitrotoluene	Blue.
2 : 4-Dinitrophenol	Yellowish-orange.
2 : 4-Dinitraniline	Red.
o-Dinitrobenzene	None.
p-Dinitrobenzene	Greenish-yellow.

Trinitro-compounds

Compound.	Colour.
1 : 3 : 5-Trinitrobenzene . .	Red.
2 : 4 : 6-Trinitrotoluene . .	Red.
2 : 4 : 6-Trinitrobenzoic acid . .	Red.
Picric acid	Orange-red.
Trinitromesitylene . . .	None.

Aldehydes

Benzidine in glacial acetic acid produces colours or precipitates with many aldehydes (Van Eck, *Centr.*, 1924, (1), 434). A saturated solution of benzidine in glacial acetic acid is diluted with an equal volume of acetic acid. A few drops of the aldehyde are added to 5 c.c. of this solution, when a coloration or precipitate is quickly obtained. Precipitates—general formula, $R{\cdot}CH{:}N{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}N{:}CH{\cdot}R$—may be crystallised and their melting points determined.

Formaldehyde . .	Faint yellow $\xrightarrow{\text{heating}}$ cherry-red.
Acetaldehyde . .	Faint yellow $\xrightarrow{\text{heating}}$ cherry-red.
Citral . . .	Deep yellow.
Benzaldehyde . .	Yellow ppt.
Anisaldehyde . .	Orange ppt.
Vanillin . . .	Orange-red ppt.
Cinnamic . . .	Blood-red colour, then ppt.
Piperonal . . .	Yellow ppt.
Salicylaldehyde . .	Yellow ppt.

Amines

Compounds containing the amino group may be detected by use of chloranil (Frehden and Goldschmidt, *Mikrochimica Acta*, 1937, 1, 347). A drop (or a few small crystals) of the compound is placed at the bottom of a small test-tube, and a couple of drops of a saturated solution of chloranil in dioxan are added. Many amines and heterocyclic compounds give a violet, blue, or red colour immediately. The test is not specific for amines, as many phenols also give colorations.

Fluorescence Analysis

Many organic compounds show characteristic fluorescence colours when exposed to ultra-violet light, and this method is used for detecting minute quantities of compounds, for detecting impurities, and as a help in separating mixtures. Thus anthracene shows an intense blue fluorescence, which disappears on the addition of the smallest trace of naphthacene, while acridine generally has a violet fluorescence due to impurities, as the pure compound has a yellow fluorescence. In separating colourless compounds by chromatographic adsorption the different layers can often be marked by examination of the column in ultra-violet light.

For further details some standard book, such as that of Radley and Grant, should be consulted.

References

Many colour tests are given in the following references.

Merck, *Reagenzien-Verzeichnis.*
Ekkert, *Erkennung organischer Verbindungen.*
Meyer, Hans, *Nachweis und Bestimmung organischer Verbindungen.*
Clarke, *Handbook of Organic Analysis.*
Radley and Grant, *Fluorescence Analysis in Ultra-violet Light.*
Danckwortt, *Lumineszenz-analyse im filtrierten Ultravioletten Licht.*

CHAPTER IV

PROPERTIES AND REACTIONS OF ORGANIC COMPOUNDS. CHOICE OF DERIVATIVES

THE chemical properties of organic compounds are largely determined by the nature of the functional groups such as CO, NH_2, COOH, etc., which are present in the molecule, and are dependent to a much smaller extent on the nature of the hydrocarbon residue, except in so far as this part of the molecule determines whether the compound is aliphatic or aromatic. It is thus possible to classify organic compounds according to the functional groups present, and to predict the properties and reactions of members of each class. An outline of such properties and reactions which are of value in qualitative work is given in this chapter.

Although the properties of organic compounds are determined by the nature of the groups present, it must be remembered that in compounds containing two or more typical groups, the latter may influence one another so that their properties cannot be so easily predicted. Thus in chlorobenzene the chlorine is not labile, but in 1-chloro-2 : 4-dinitrobenzene it is very reactive, due to the presence of nitro groups in the *ortho* and *para* positions. In most of the compounds dealt with in this book the groups retain their identity and are little influenced by the presence of neighbouring groups.

Derivatives suitable for the identification of various classes of compounds are given in the following pages under the appropriate headings. Details for the preparations of these derivatives will be found in Chapter V.

HYDROCARBONS

Saturated Hydrocarbons

These compounds have few characteristic chemical properties and are very inert. Thus the paraffins and the cyclic compounds

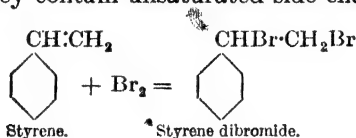
such as cyclohexane are insoluble in concentrated sulphuric acid, and are not attacked by cold fuming nitric acid—a vigorous reagent which attacks most organic compounds. In their stability the saturated hydrocarbons resemble the ethers. The two classes of compounds may be distinguished by their behaviour to iodine, which dissolves in hydrocarbons to give a violet colour and in ethers to give a brown colour.

Unsaturated Hydrocarbons

The aliphatic and alicyclic unsaturated compounds readily decolorise a solution of bromine in glacial acetic acid or carbon tetrachloride, bromine adding on to the double bond to give, in many cases, crystalline products.

$$\underset{\text{Ethylene.}}{\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix}} + Br_2 = \underset{\text{Ethylene dibromide.}}{\begin{matrix} CH_2Br \\ | \\ CH_2Br \end{matrix}}$$

Many terpenes contain double bonds, but the formation of di- and tetra-bromo derivatives is often a matter of difficulty, especially in small-scale work. Aromatic compounds do not respond to this test unless they contain unsaturated side-chains—*e.g.*:

$$\underset{\text{Styrene.}}{C_6H_5 \cdot CH{:}CH_2} + Br_2 = \underset{\text{Styrene dibromide.}}{C_6H_5 \cdot CHBr \cdot CH_2Br}$$

Unsaturated compounds decolorise solutions of potassium permanganate instantly (Baeyer's test) to give a brown solution or precipitate. Other compounds such as aldehydes reduce permanganate, but more slowly.

In many cases, especially in the aliphatic series, members of this class of compound are identified by their physical properties.

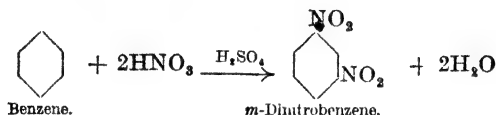
Aromatic Hydrocarbons

The aromatic hydrocarbons are insoluble in concentrated sulphuric acid, but they react briskly with cold fuming nitric acid. Crystalline derivatives are obtained by nitration, by the

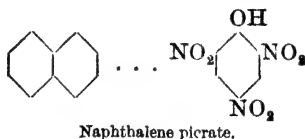
formation of molecular compounds with polynitro-compounds such as picric acid, and in the case of compounds with side-chains by oxidation to carboxylic acids. Some hydrocarbons can be identified by oxidation to quinones with chromic acid in glacial acetic acid.

Nitrations are generally performed with a mixture of nitric acid and sulphuric acid, the nature of the products depending on the strengths of the acids used.

$$C_6H_6 + 2HNO_3 \xrightarrow{H_2SO_4} C_6H_4(NO_2)_2 + 2H_2O$$

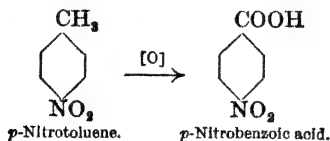
Benzene. *m*-Dinitrobenzene.

The molecular compounds formed by the interaction of picric acid with aromatic hydrocarbons are highly coloured products which crystallise readily. Some of them decompose when crystallised from alcohol or on exposure to air.

$$C_{10}H_8 \ldots C_6H_2(OH)(NO_2)_3$$

Naphthalene picrate.

Many other nitro compounds—2 : 4 : 6-trinitrobenzene, *m*-dinitrobenzene, picramide, etc.—also give molecular compounds.

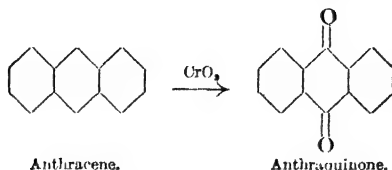
Side-chains in aromatic compounds are oxidised to carboxyl groups by potassium permanganate commonly in alkaline solution.

$$CH_3 \cdot C_6H_4 \cdot NO_2 \xrightarrow{[O]} COOH \cdot C_6H_4 \cdot NO_2$$

p-Nitrotoluene. *p*-Nitrobenzoic acid.

The rate of oxidation depends on a number of factors, including the nature of the hydrocarbon; iodo-toluenes, for example, are oxidised exceedingly slowly by potassium permanganate, and are best oxidised by dilute nitric acid.

Condensed aromatic hydrocarbons are often oxidised to quinones by chromic acid in glacial acetic acid.

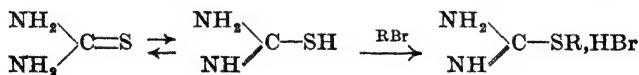
$$\text{Anthracene} \xrightarrow{CrO_3} \text{Anthraquinone}$$

Anthracene. Anthraquinone.

Quinones are easily purified by crystallisation from glacial acetic acid or by sublimation, but some are not readily obtained in the pure state.

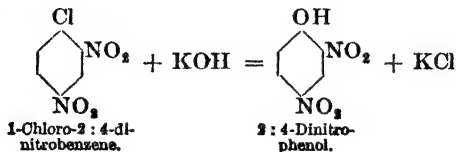
Colour tests are sometimes a help in detecting aromatic hydrocarbons (see p. 44). A reagent which has recently been used for this purpose is iodic acid (Masson and Race, *J.*, 1937, 1718).

Halogen Derivatives of the Hydrocarbons

Halogen compounds in the aliphatic series yield potassium halides on gentle heating with alcoholic potassium hydroxide: alcoholic silver nitrate reacts similarly. In the case of the iodo compounds it must be remembered that potassium iodide is soluble in alcohol. The bromides and iodides and some chlorides react with thiourea to give salts of alkyl-*iso*thioureas which form crystalline picrates (cf. Sidgwick, *Chemistry of Nitrogen*, p. 290).

$$(NH_2)_2C{=}S \rightleftarrows NH_2(NH{=})C{-}SH \xrightarrow{RBr} NH_2(NH{=})C{-}SR,HBr$$

Aromatic compounds with halogen in the side-chain react similarly with potassium hydroxide and with thiourea. If the halogen is attached directly to the nucleus it is not attacked by potassium hydroxide except in the case of certain nitro-compounds, where the nitro-groups are situated *ortho* and *para* to the halogen atom.

$$C_6H_3Cl(NO_2)_2 + KOH = C_6H_3(OH)(NO_2)_2 + KCl$$

1-Chloro-2 : 4-dinitrobenzene. 2 : 4-Dinitrophenol.

Crystalline derivatives are obtained, as in the case of the aromatic hydrocarbons, by nitration, molecular compound formation, and side-chain oxidation.

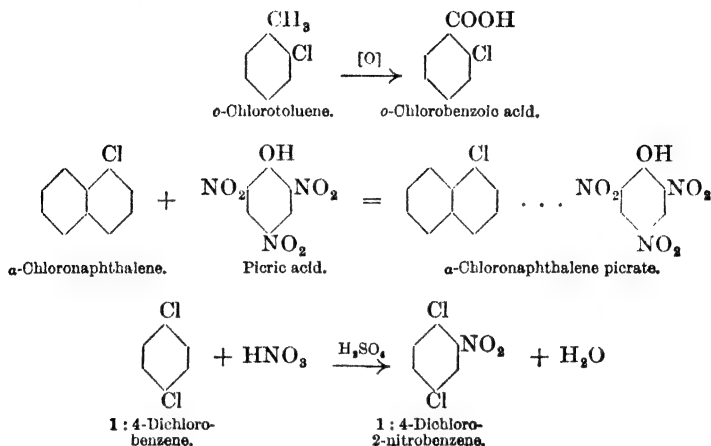
$$\text{CH}_3\text{C}_6\text{H}_4\text{Cl} \xrightarrow{[O]} \text{COOH}\cdot\text{C}_6\text{H}_4\text{Cl}$$

o-Chlorotoluene. *o*-Chlorobenzoic acid.

$$\text{C}_{10}\text{H}_7\text{Cl} + \text{HO}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3 = \text{C}_{10}\text{H}_7\text{Cl} \ldots \text{HO}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3$$

α-Chloronaphthalene. Picric acid. α-Chloronaphthalene picrate.

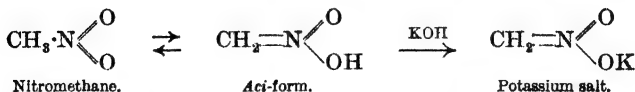
$$\text{C}_6\text{H}_4\text{Cl}_2 + \text{HNO}_3 \xrightarrow{\text{H}_2\text{SO}_4} \text{C}_6\text{H}_3\text{Cl}_2\text{NO}_2 + \text{H}_2\text{O}$$

1 : 4-Dichloro-benzene. 1 : 4-Dichloro-2-nitrobenzene.

Nitro-Compounds

A distinction must be made between nitro-compounds and nitrites, which have the general formula R—O—N=O and are esters which can be hydrolysed. True nitro-compounds cannot be hydrolysed.

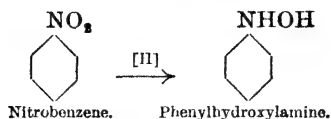
The aliphatic nitro-compounds and aromatic compounds with the nitro-group in the side-chain react with alcoholic potassium hydroxide to give potassium salts of pseudo acids.

$$\text{CH}_3\cdot\text{N}\begin{matrix}\nearrow\text{O}\\ \searrow\text{O}\end{matrix} \rightleftarrows \text{CH}_2{=}\text{N}\begin{matrix}\nearrow\text{O}\\ \diagdown\text{OH}\end{matrix} \xrightarrow{\text{KOH}} \text{CH}_2{=}\text{N}\begin{matrix}\nearrow\text{O}\\ \diagdown\text{OK}\end{matrix}$$

Nitromethane. *Aci*-form. Potassium salt.

The nitro-compounds readily undergo reduction to amines, and thus react with tin and hydrochloric acid to give clear solutions of the amine hydrochlorides. Other compounds such as azo-benzene react similarly, but may easily be differentiated (see p. 36). Reduction with zinc dust in the presence of calcium

chloride yields hydroxylamine derivatives, which are readily detected by their reducing action on ammoniacal silver nitrate.

$$C_6H_5NO_2 \xrightarrow{[H]} C_6H_5NHOH$$

Nitrobenzene. Phenylhydroxylamine.

Crystalline derivatives are made by reduction to amino-compounds, which are identified by acetylation and benzoylation; by further nitration to polynitro-compounds; by combination with aromatic hydrocarbons to give molecular compounds; and by oxidation to substituted benzoic acids.

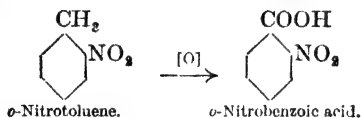
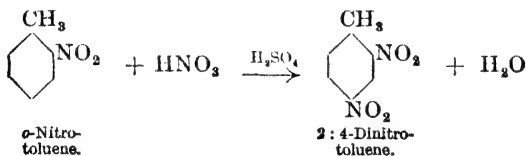
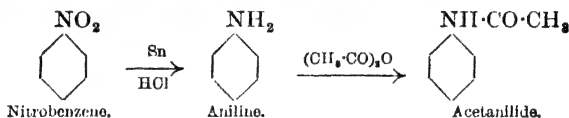
$$C_6H_5NO_2 \xrightarrow[HCl]{Sn} C_6H_5NH_2 \xrightarrow{(CH_3{\cdot}CO)_2O} C_6H_5NH{\cdot}CO{\cdot}CH_3$$

Nitrobenzene. Aniline. Acetanilide.

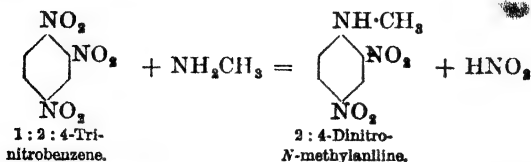
$$CH_3{\cdot}C_6H_4{\cdot}NO_2 + HNO_3 \xrightarrow{H_2SO_4} CH_3{\cdot}C_6H_3(NO_2)_2 + H_2O$$

o-Nitrotoluene. 2 : 4-Dinitrotoluene.

$$CH_2{\cdot}C_6H_4{\cdot}NO_2 \xrightarrow{[O]} COOH{\cdot}C_6H_4{\cdot}NO_2$$

o-Nitrotoluene. *o*-Nitrobenzoic acid.

In certain instances derivatives can be prepared by replacement reactions. Thus 1 : 2 : 4-trinitrobenzene reacts immediately in alcoholic solution with amines to give N-substituted-dinitroanilines.

$$C_6H_3(NO_2)_3 + NH_2CH_3 = NH{\cdot}CH_3{\cdot}C_6H_3(NO_2)_2 + HNO_2$$

1 : 2 : 4-Trinitrobenzene. 2 : 4-Dinitro-*N*-methylaniline.

Colour tests for nitro-compounds are given on p. 45.

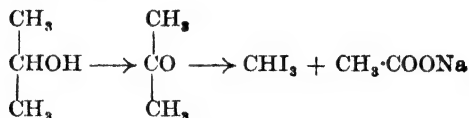
Hydroxylic-Compounds

The hydroxy-compounds are divided into two main groups—alcohols and phenols. The phenols are aromatic, but the alcohols may be either aliphatic or aromatic. Whereas the alcohols are neutral in reaction, the phenols are weakly acidic.

Alcohols

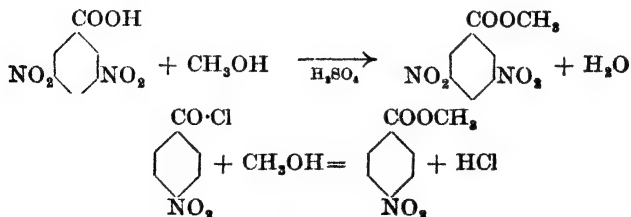
Many of the alcohols are liquids with pleasant odours. They react with sodium to give alcoholates and with phosphorus pentachloride to form chloro-derivatives. Ethers are easily distinguished from the alcohols, as they are non-reactive to both sodium and phosphorus pentachloride.

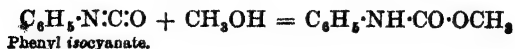
Many alcohols give the iodoform test, as they are oxidised first by the sodium hypoiodite to aldehydes or ketones, which in turn yield iodoform.

$$CH_3\cdot CHOH\cdot CH_3 \longrightarrow CH_3\cdot CO\cdot CH_3 \longrightarrow CHI_3 + CH_3\cdot COONa$$

Crystalline derivatives are available for the identification of the alcohols, the more important ones being the following:

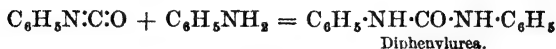
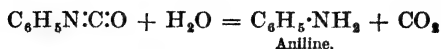
With suitable acids and acid chlorides crystalline esters are formed. 3 : 5-Dinitrobenzoic acid and *p*-nitrobenzoyl chloride are commonly used.

$$C_6H_3(NO_2)_2\cdot COOH + CH_3OH \xrightarrow{H_2SO_4} C_6H_3(NO_2)_2\cdot COOCH_3 + H_2O$$

$$NO_2\cdot C_6H_4\cdot CO\cdot Cl + CH_3OH = NO_2\cdot C_6H_4\cdot COOCH_3 + HCl$$

*Iso*cyanates react immediately with alcohols giving good yields of substituted urethanes.

$$\underset{\text{Phenyl isocyanate.}}{C_6H_5\cdot N{:}C{:}O} + CH_3OH = C_6H_5\cdot NH\cdot CO\cdot OCH_3$$

Water must not be present: otherwise substituted ureas are formed.

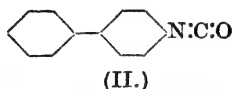
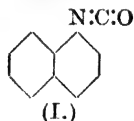
$$C_6H_5N{:}C{:}O + H_2O = C_6H_5{\cdot}NH_2 + CO_2$$
Aniline.

$$C_6H_5N{:}C{:}O + C_6H_5NH_2 = C_6H_5{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_6H_5$$
Diphenylurea.

Phenyl *iso*cyanate is the reagent generally used, but it has the disadvantage that it does not keep well, as it reacts with atmospheric moisture. α-Naphthyl *iso*cyanate (I) and 4-diphenylyl *iso*cyanate (II) are to be preferred, as they are much less sensitive to moisture.

N:C:O

(I.)

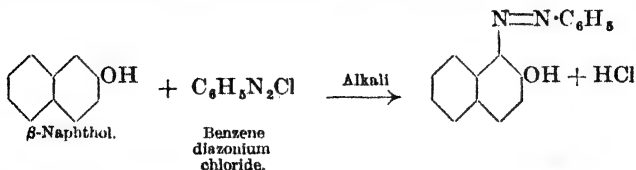
N:C:O

(II.)

Phenols

Phenols like the carboxylic acids are soluble in sodium hydroxide solution, but differ in being insoluble in sodium bicarbonate solution. Acids and phenols may therefore be separated by dissolving them in caustic soda solution, and passing in a current of carbon dioxide. Only the phenols are precipitated.

A number of colour reactions are used to detect phenols. Characteristic colorations are given with ferric chloride in aqueous or alcoholic solution, though substituted phenols such as *o*-nitrophenol do not respond to the test. The Liebermann reaction is also used to detect phenols as well as nitroso-compounds. Brilliantly coloured precipitates of azo dyes are obtained when the phenols couple in alkaline solution with diazotised amines.

$$\text{OH} + C_6H_5N_2Cl \xrightarrow{\text{Alkali}} (N{=}N{\cdot}C_6H_5)\text{OH} + HCl$$

β-Naphthol. Benzene diazonium chloride.

Characteristic colours are often obtained by the phthalein test, in which a phenol is fused with phthalic anhydride in presence

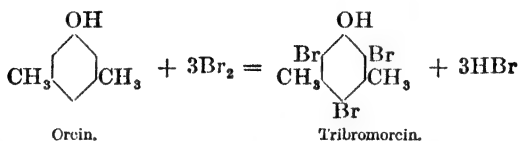
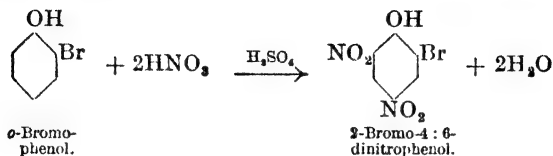
of a little zinc chloride and the melt treated with sodium hydroxide solution.

The presence of the hydroxyl group in the ring facilitates nitration and halogenation, and the resulting compounds are useful for identification.

$$C_6H_4(OH)Br + 2HNO_3 \xrightarrow{H_2SO_4} C_6H_2(OH)Br(NO_2)_2 + 2H_2O$$

o-Bromophenol. 2-Bromo-4 : 6-dinitrophenol.

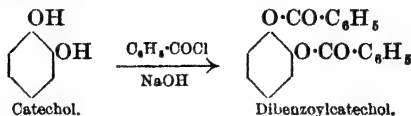
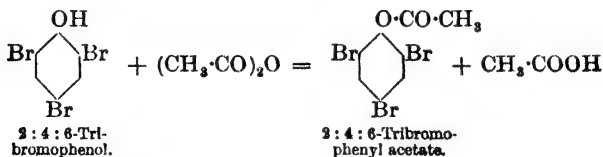
$$C_6H_3(OH)(CH_3)_2 + 3Br_2 = C_6Br_3(OH)(CH_3)_2 + 3HBr$$

Orcin. Tribromorcin.

Many other derivatives are available, the commonest being the acetyl and benzoyl derivatives. The former are prepared by means of acetic anhydride containing a trace of sulphuric acid or by acetyl chloride, while the latter are formed with benzoyl chloride in alkaline solution (Schotten–Baumann reaction). The benzoyl compounds are to be preferred, as they can be prepared in the presence of moisture, which interferes with the use of acetylation reagents such as acetic anhydride or acetyl chloride.

$$C_6H_2Br_3(OH) + (CH_3{\cdot}CO)_2O = C_6H_2Br_3(O{\cdot}CO{\cdot}CH_3) + CH_3{\cdot}COOH$$

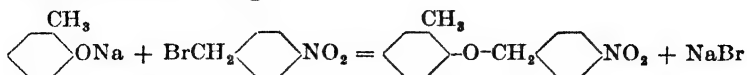
2 : 4 : 6-Tribromophenol. 2 : 4 : 6-Tribromophenyl acetate.

$$C_6H_4(OH)_2 \xrightarrow[NaOH]{C_6H_5{\cdot}COCl} C_6H_4(O{\cdot}CO{\cdot}C_6H_5)_2$$

Catechol. Dibenzoylcatechol.

p-Nitrobenzoyl chloride can be used with advantage instead of benzoyl chloride, as it gives derivatives with higher melting points.

p-Nitrobenzyl bromide has recently been introduced as a

reagent for the identification of phenols. Ethers are very easily formed with this compound.

$$CH_3C_6H_4ONa + BrCH_2C_6H_4NO_2 = CH_3C_6H_4{-}O{-}CH_2C_6H_4NO_2 + NaBr$$

Another method which has been recently introduced is the formation of aryloxyacetic acids by the action of chloracetic acid on phenols.

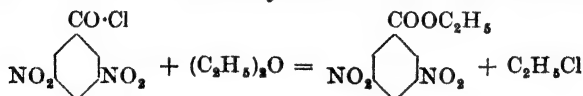
$$C_6H_5OH + Cl{\cdot}CH_2{\cdot}COOH = C_6H_5{\cdot}O{\cdot}CH_2{\cdot}COOH + HCl$$

Both the melting points and the neutralisation equivalents of these acids are determined in order to establish their identity.

Ethers

The ethers are very stable substances. They are readily distinguished from the aromatic hydrocarbons, as they are soluble in cold concentrated sulphuric acid (see also p. 49), and differ from the alcohols by not reacting with sodium or phosphorus pentachloride.

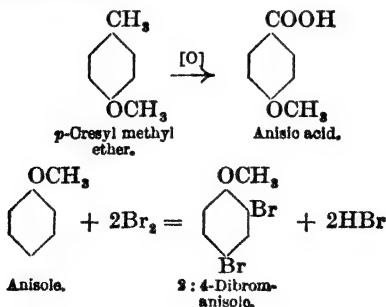
The only method of preparing derivatives of the aliphatic ethers is that of Underwood, Baril, and Toone (*J. Amer. Chem. Soc.*, 1930, **52**, 4087), in which esters are formed by heating ethers with 3 : 5-dinitrobenzoyl chloride and zinc chloride.

$$(NO_2)_2C_6H_3{\cdot}CO{\cdot}Cl + (C_2H_5)_2O = (NO_2)_2C_6H_3{\cdot}COOC_2H_5 + C_2H_5Cl$$

Derivatives of the aromatic ethers are generally obtained by oxidation or bromination.

$$CH_3{\cdot}C_6H_4{\cdot}OCH_3 \xrightarrow{[O]} COOH{\cdot}C_6H_4{\cdot}OCH_3$$

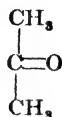
p-Cresyl methyl ether. → Anisic acid.

$$C_6H_5OCH_3 + 2Br_2 = C_6H_3Br_2OCH_3 + 2HBr$$

Anisole. → 2 : 4-Dibromanisole.

Carbonyl Compounds

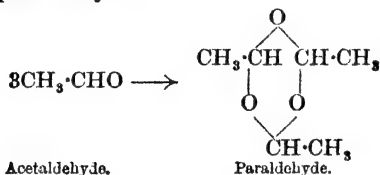
To this class of compound belong the aldehydes, ketones, and quinones.

CH_3–C(=O)H Acetaldehyde.

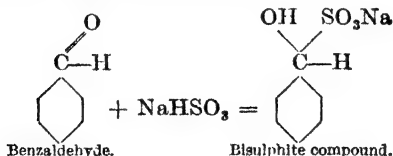
CH_3–C(=O)–CH_3 Acetone.

O=C$_6$H$_4$=O Benzoquinone.

Aldehydes and Ketones

The aldehydes are among the most reactive of organic compounds. Thus acetaldehyde polymerises readily with sulphuric acid to form paraldehyde.

$$3CH_3\cdot CHO \longrightarrow (CH_3\cdot CH\cdot O)_3$$

Acetaldehyde. Paraldehyde.

The compounds formed when aldehydes and some ketones are treated with a freshly prepared solution of sodium bisulphite are exceedingly useful for separating aldehydes from other organic compounds, as they mostly separate in a crystalline mass which is insoluble in organic solvents. On treatment with acid or alkali they decompose to give the aldehyde.

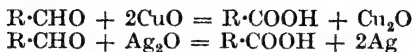
$$C_6H_5\cdot CHO + NaHSO_3 = C_6H_5\cdot CH(OH)SO_3Na$$

Benzaldehyde. Bisulphite compound.

Aldehydes and ketones containing the $CH_3\cdot CO$ group give iodoform on treatment with iodine and caustic soda solution.

$$CH_3\cdot CHO + 3I_2 + 4NaOH = CHI_3 + H\cdot COONa + 3NaI + 3H_2O$$

A modification of the test using dioxan as solvent has been advocated by Fuson and Tullock (*J. Amer. Chem. Soc.*, 1934, **56**. 1638).

Aldehydes are distinguished from ketones in several ways, most of which make use of the fact that aldehydes, in contrast to ketones, are reducing agents. Thus aldehydes reduce Fehling's solution to red cuprous oxide and Tollen's solution to silver, while ketones do not do so.

$$R\cdot CHO + 2CuO = R\cdot COOH + Cu_2O$$
$$R\cdot CHO + Ag_2O = R\cdot COOH + 2Ag$$

In the second test the silver can be obtained in the form of a bright mirror. It must be pointed out, however, that under ordinary conditions aromatic aldehydes such as benzaldehyde do not reduce Fehling's solution.

Aldehydes reduce alkaline potassium permanganate to manganese dioxide.

Aldehydes react characteristically with Schiff's reagent by restoring the colour of the solution. Some of the aromatic aldehydes restore the colour slowly. Certain ketones also restore the colour slowly, while samples of ketones sometimes restore the colour owing to small quantities of aldehydes being present. This is a good example of the need for care in drawing conclusions from colour tests.

There are many reagents for the detection and identification of aldehydes and ketones, the most important of which are the following ammonia derivatives—hydroxylamine, semicarbazide, phenylhydrazine, and 2 : 4-dinitrophenylhydrazine. The first two reagents are generally used in the form of their hydrochlorides.

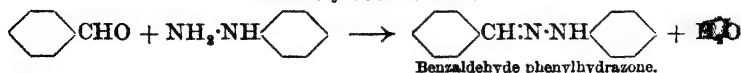
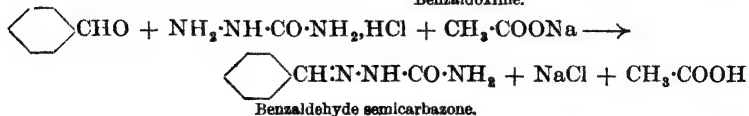
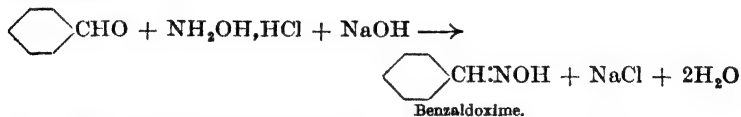
$$C_6H_5\cdot CHO + NH_2OH,HCl + NaOH \longrightarrow C_6H_5\cdot CH{:}NOH + NaCl + 2H_2O$$

Benzaldoxime.

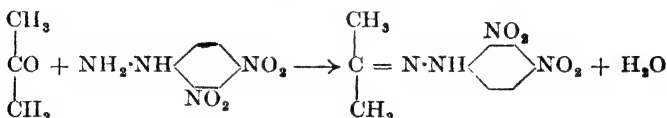
$$C_6H_5\cdot CHO + NH_2\cdot NH\cdot CO\cdot NH_2,HCl + CH_3\cdot COONa \longrightarrow C_6H_5\cdot CH{:}N\cdot NH\cdot CO\cdot NH_2 + NaCl + CH_3\cdot COOH$$

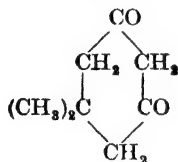
Benzaldehyde semicarbazone.

$$C_6H_5\cdot CHO + NH_2\cdot NH\cdot C_6H_5 \longrightarrow C_6H_5\cdot CH{:}N\cdot NH\cdot C_6H_5 + H_2O$$

Benzaldehyde phenylhydrazone.

The oximes and semicarbazones are not ideal compounds for identification purposes. Theoretically each oxime may exist in

two forms—*syn* and *anti*—while the semicarbazones often take many hours to prepare, and their melting points are sometimes dependent on factors such as the rate of heating. Phenylhydrazine is of general application, but the most useful reagent is 2 : 4-dinitrophenylhydrazine, the value of which was first emphasised by Brady (*Analyst*, 1926, **51**, 77). With aldehydes and ketones this reagent gives hydrazones. The crystalline nature of these hydrazones and their low solubility in the common organic solvents are of material assistance in their preparation and purification. For example, acetone with phenylhydrazine gives an oily phenylhydrazone, but with dinitrophenylhydrazine a crystalline dinitrophenylhydrazone is easily obtained.

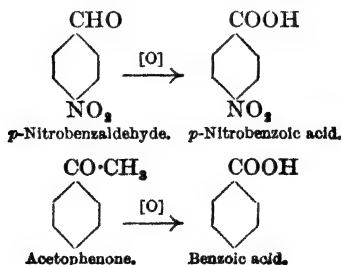
$$(CH_3)_2CO + NH_2{\cdot}NH{\cdot}C_6H_3(NO_2)_2 \longrightarrow (CH_3)_2C{=}N{\cdot}NH{\cdot}C_6H_3(NO_2)_2 + H_2O$$

5 : 5-Dimethyldihydroresorcinol (dimedone) very readily forms crystalline derivatives with aldehydes, and is suitable for micro work.

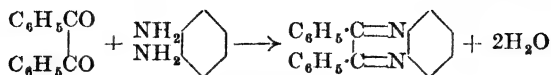
$$\text{CO}\langle\text{CH}_2\text{—C(CH}_3)_2\text{—CH}_2\text{—CO—CH}_2\rangle$$

Aldehydes and ketones are oxidised by potassium permanganate to acids. This is specially useful in the aromatic series, where the resulting acids are easily obtained in the crystalline state.

$$p\text{-}NO_2{\cdot}C_6H_4{\cdot}CHO \xrightarrow{[O]} p\text{-}NO_2{\cdot}C_6H_4{\cdot}COOH$$

p-Nitrobenzaldehyde. *p*-Nitrobenzoic acid.

$$C_6H_5{\cdot}CO{\cdot}CH_3 \xrightarrow{[O]} C_6H_5{\cdot}COOH$$

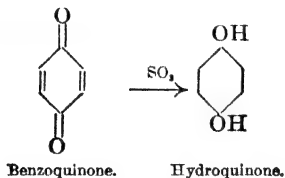
Acetophenone. Benzoic acid.

Diketones such as benzil form quinoxalines with *ortho*-phenylenediamine.

$$\begin{matrix} C_6H_5CO \\ | \\ C_6H_5CO \end{matrix} + \begin{matrix} NH_2 \\ NH_2 \end{matrix} C_6H_4 \longrightarrow \begin{matrix} C_6H_5 \cdot C{=}N \\ | \\ C_6H_5 \cdot C{=}N \end{matrix} C_6H_4 + 2H_2O$$

Quinones

The quinones are coloured compounds, many of which are volatile in steam, while many can be purified by sublimation. Although they contain the carbonyl group, they do not always react with the standard carbonyl reagents in normal fashion. Thus benzoquinone is reduced by phenylhydrazine.

Some of the quinones are reduced by sulphurous acid to the corresponding phenols, but others are not attacked by this reagent. Thus benzoquinone is reduced to hydroquinone, while anthraquinone is unaffected by sulphurous acid.

$$O{=}C_6H_4{=}O \xrightarrow{SO_2} HO{-}C_6H_4{-}OH$$

Benzoquinone. Hydroquinone.

Each quinone must therefore be identified by its own particular reactions. For instance, phenanthraquinone is identified by the green colour it gives with concentrated sulphuric acid, and by the quinoxaline it forms with *o*-phenylenediamine.

Carbohydrates

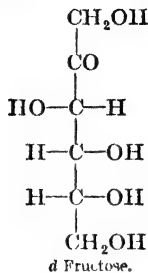
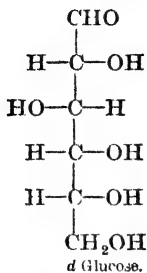
The carbohydrates are divided into three classes

Monosaccharides, *e.g.*, glucose.
Disaccharides, *e.g.*, maltose, sucrose.
Polysaccharides, *e.g.*, starch.

The monosaccharides are either aldoses (polyhydroxy aldehydes) such as glucose, or ketoses (polyhydroxy ketones) such as fructose.

The open-chain formulæ are given below, but it must be remembered that though such structures are useful in depicting

$$
\begin{array}{c}
\mathrm{CHO} \\
| \\
\mathrm{H-C-OH} \\
| \\
\mathrm{HO-C-H} \\
| \\
\mathrm{H-C-OH} \\
| \\
\mathrm{H-C-OH} \\
| \\
\mathrm{CH_2OH}
\end{array}
\qquad\qquad
\begin{array}{c}
\mathrm{CH_2OH} \\
| \\
\mathrm{CO} \\
| \\
\mathrm{HO-C-H} \\
| \\
\mathrm{H-C-OH} \\
| \\
\mathrm{H-C-OH} \\
| \\
\mathrm{CH_2OH}
\end{array}
$$

d Glucose. *d* Fructose.

the reactions of the sugars, they are not believed to have more than an ephemeral existence, the compounds normally occurring in cyclic forms. It should also be noted that the letters *d*- and *l*- do not refer to the sign of the optical rotation of the sugars, but to their structure.

The disaccharides are derived by the elimination of one molecule of water from two molecules of monosaccharides, and on hydrolysis with mineral acids they yield monosaccharides.

The polysaccharides are complex carbohydrates such as starch and cellulose, which likewise break down on hydrolysis into monosaccharides.

Properties of the Carbohydrates

Sugars such as glucose and sucrose are very soluble in water, but the polysaccharides in general are much less soluble. Most carbohydrates decompose on heating, and do not have sharp melting points. Sugars are optically active, and may be identified by this means. Mutarotation is observed with many sugars in solution.

Reducing sugars give yellow colorations when heated with sodium hydroxide solution.

The violet colour produced with Molisch's reagent is frequently employed to detect carbohydrates.

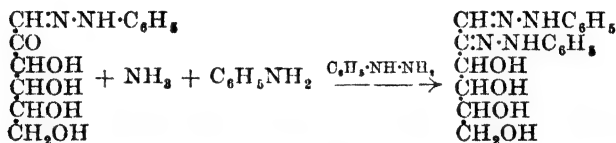
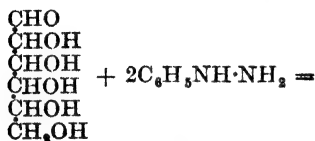
For identification purposes the sugars may be divided into two groups: reducing sugars and non-reducing sugars. The former give a precipitate of silver with ammoniacal silver nitrate

(Tollen's reagent) and of cuprous oxide with alkaline copper sulphate solution (Fehling's solution). A further division is obtained by testing with copper acetate in dilute acetic acid (Barfoed's reagent); monosaccharides give a red precipitate of cuprous oxide whilst the disaccharides give no precipitate.

Fehling's solution +	+	—
Barfoed's reagent +	—	—
d-Fructose . . . . *d*-Mannose . . . . *d*-Xylose . . . . *d*-Glucose . . . . *d*-Galactose . . . *l*-Arabinose . . .	Maltose Lactose	Sucrose

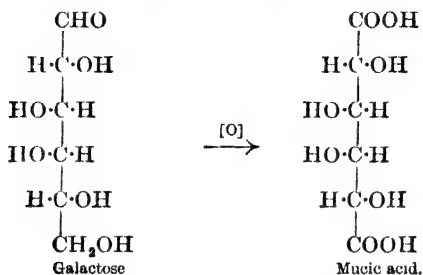
All monosaccharides and some disaccharides form osazones with phenylhydrazine in acetic acid solution.

$$\begin{array}{l} CHO \\ CHOH \\ CHOH \\ CHOH \\ CHOH \\ CH_2OH \end{array} + 2C_6H_5NH{\cdot}NH_2 =$$

$$\begin{array}{l} CH{:}N{\cdot}NH{\cdot}C_6H_5 \\ CO \\ CHOH \\ CHOH \\ CHOH \\ CH_2OH \end{array} + NH_3 + C_6H_5NH_2 \xrightarrow{C_6H_5{\cdot}NH{\cdot}NH_2} \begin{array}{l} CH{:}N{\cdot}NHC_6H_5 \\ C{:}N{\cdot}NHC_6H_5 \\ CHOH \\ CHOH \\ CHOH \\ CH_2OH \end{array}$$

The osazones separate from solution in yellow crystals which exhibit characteristic forms of aggregation under the microscope. Under standard conditions the time necessary for precipitation of the osazones is specific for each sugar, and may be used for identification of the sugars.

The approximate melting points of the sugars and the crystalline appearance and melting points of their osazones are the properties used for identification. It should be stated, however, that the melting points of the osazones are not always satisfactory, the osazones of several sugars melting at practically the same temperature.

Galactose and lactose are differentiated from other reducing sugars by yielding mucic acid on oxidation with nitric acid.

```
     CHO                              COOH
      |                                 |
   H·C·OH                            H·C·OH
      |                                 |
  HO·C·H                            HO·C·H
      |              [O]                |
  HO·C·H           ------>          HO·C·H
      |                                 |
   H·C·OH                            H·C·OH
      |                                 |
     CH2OH                            COOH
   Galactose                        Mucic acid.
```

Aldoses and Ketoses

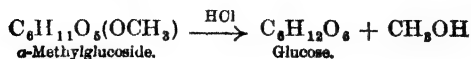
Aldoses may be distinguished from ketoses in two ways. Aldoses are quickly oxidised by bromine water to acids and consequently rapidly decolorise bromine water. Ketoses, on the other hand, are resistant to this reagent. A more positive test for ketoses is the deep red colour which they give with Seliwanoff's reagent (see Appendix). Ketoses produce the colour rapidly; aldoses do so only after heating for some time.

Pentoses

Characteristic colorations are given by pentoses with orcinol and hydrochloric acid (Bial's reagent), and with phloroglucinol and hydrochloric acid (Tollens' reagent).

Glycosides

The simplest members of this class are the α- and β-methylglucosides. They are crystalline compounds which in many cases are readily detected by the brilliant colours they give with concentrated sulphuric acid. They also give Molisch's reaction, but do not reduce Fehling's solution or form osazones. On boiling with dilute hydrochloric acid they are broken up into their components.

$$\underset{\alpha\text{-Methylglucoside.}}{C_6H_{11}O_5(OCH_3)} \xrightarrow{HCl} \underset{\text{Glucose.}}{C_6H_{12}O_6} + CH_3OH$$

Carboxylic Acids

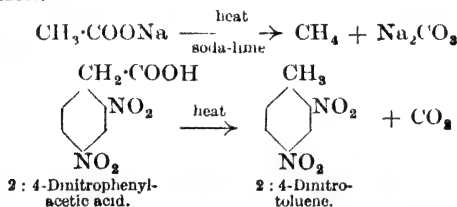
The simple aliphatic carboxylic acids are soluble in cold water giving solutions acid to litmus, but the higher homologues and many of the aromatic acids are practically insoluble. The acids dissolve in caustic soda solution, and in the case of the aromatic compounds the free acids separate in the crystalline state when mineral acid is added to aqueous solutions of their salts.

Ferric chloride gives characteristic colours with salts of the acids :

Aromatic acids, buff-coloured precipitate.
Aliphatic acids, reddish-brown colour.
α-Hydroxy acids, yellow colour.

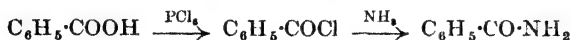
Carboxylic acids lose CO_2 on being heated with soda–lime; a few of them undergo this change merely on being heated alone or in solution.

$$CH_3{\cdot}COONa \xrightarrow[\text{soda-lime}]{\text{heat}} CH_4 + Na_2CO_3$$

$$\underset{\text{2 : 4-Dinitrophenylacetic acid.}}{(NO_2)_2C_6H_3{\cdot}CH_2{\cdot}COOH} \xrightarrow{\text{heat}} \underset{\text{2 : 4-Dinitrotoluene.}}{(NO_2)_2C_6H_3{\cdot}CH_3} + CO_2$$

These products can be purified and identified.

Some of the derivatives used to identify acids are given below.

The acid amides, easily obtained by way of the acid chlorides, are suitable for the aromatic acids, but not for the aliphatic, the amides of the latter being too readily soluble in water.

$$C_6H_5{\cdot}COOH \xrightarrow{PCl_5} C_6H_5{\cdot}COCl \xrightarrow{NH_3} C_6H_5{\cdot}CO{\cdot}NH_2$$

Acids in the form of their sodium salts can be readily converted by means of *p*-nitrobenzyl bromide into crystalline *p*-nitrobenzyl esters. Another useful method is the identification as *S*-benzylthioronium salts (Donleavy, *J. Amer. Chem. Soc.*, 1936, **58**, 1004).

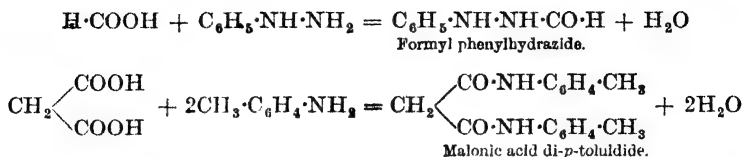
Phenylhydrazides and *p*-toluidides are formed by heating acids with phenylhydrazine and *p*-toluidine respectively. The

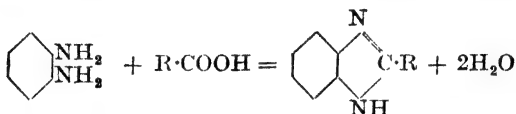
p-toluidides are specially suitable for identifying the dibasic acids.

$$H\cdot COOH + C_6H_5\cdot NH\cdot NH_2 = C_6H_5\cdot NH\cdot NH\cdot CO\cdot H + H_2O$$

Formyl phenylhydrazide.

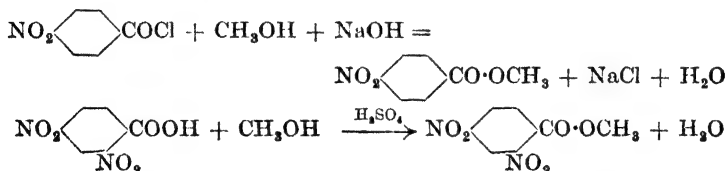
$$CH_2\begin{cases}COOH \\ COOH\end{cases} + 2CH_3\cdot C_6H_4\cdot NH_2 = CH_2\begin{cases}CO\cdot NH\cdot C_6H_4\cdot CH_3 \\ CO\cdot NH\cdot C_6H_4\cdot CH_3\end{cases} + 2H_2O$$

Malonic acid di-*p*-toluidide.

Aliphatic acids may be quickly identified by the 2-alkylbenziminazole picrates. These are formed by the action of the acids on *o*-phenylenediamine in the presence of hydrochloric acid, and treating the compound so obtained with picric acid.

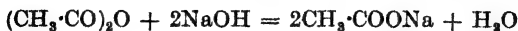
$$C_6H_4(NH_2)_2 + R\cdot COOH = C_6H_4\begin{cases}N \\ NH\end{cases}C\cdot R + 2H_2O$$

Aromatic acids frequently form crystalline methyl esters either by the Schotten–Baumann method or by the Fischer-Speier method.

$$NO_2C_6H_4COCl + CH_3OH + NaOH =$$

$$NO_2C_6H_4CO\cdot OCH_3 + NaCl + H_2O$$

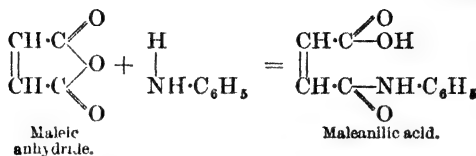
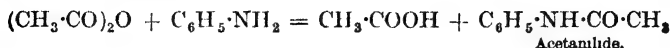
$$(NO_2)_2C_6H_3COOH + CH_3OH \xrightarrow{H_2SO_4} (NO_2)_2C_6H_3CO\cdot OCH_3 + H_2O$$

Acid Anhydrides

Most of the anhydrides on boiling with water for a few seconds give a solution acid to litmus, but some are comparatively stable to water. On boiling with caustic soda salts of the corresponding acids are obtained which may be identified by means of *p*-nitrobenzyl bromide (see p. 90).

$$(CH_3\cdot CO)_2O + 2NaOH = 2CH_3\cdot COONa + H_2O$$

The anhydrides are more reactive than the acids, and advantage is taken of this fact in their identification. For instance,

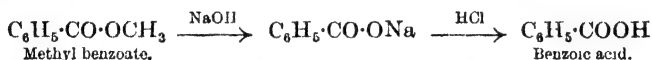
they react immediately with aniline to give anilides, or in the case of the dibasic acids, anilic acids.

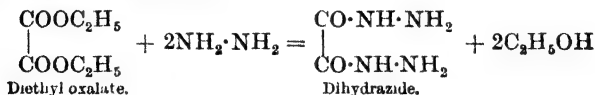
$$(CH_3\cdot CO)_2O + C_6H_5\cdot NH_2 = CH_3\cdot COOH + \underset{\text{Acetanilide.}}{C_6H_5\cdot NH\cdot CO\cdot CH_3}$$

$$\underset{\text{Maleic anhydride.}}{\begin{matrix} CH\cdot C{=}O \\ \| \quad\quad >O \\ CH\cdot C{=}O \end{matrix}} + \begin{matrix} H \\ | \\ NH\cdot C_6H_5 \end{matrix} = \underset{\text{Maleanilic acid.}}{\begin{matrix} CH\cdot C(=O)-OH \\ \| \\ CH\cdot C(=O)-NH\cdot C_6H_5 \end{matrix}}$$

p-Toluidine can often be used with advantage instead of aniline, *p*-toluidides being obtained.

Esters

Many of the esters are sweet-smelling liquids, but esters of aromatic acids are frequently solids. Esters are hydrolysed by aqueous or alcoholic sodium hydroxide to alcohols and acids, and this is a common means of identification, especially in the aromatic series, where the acids are readily obtained in the crystalline state.

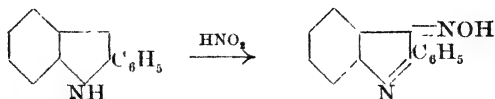
$$\underset{\text{Methyl benzoate.}}{C_6H_5\cdot CO\cdot OCH_3} \xrightarrow{NaOH} C_6H_5\cdot CO\cdot ONa \xrightarrow{HCl} \underset{\text{Benzoic acid.}}{C_6H_5\cdot COOH}$$

Some of the simpler esters are hydrolysed in aqueous solution, formic acid, for example, being readily detected in aqueous solutions of methyl formate. Such esters readily form hydrazides, 2-alkylbenziminazoles, etc.

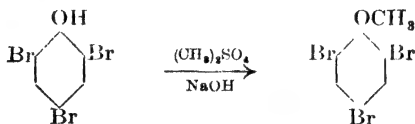
$$\underset{\text{Diethyl oxalate.}}{\begin{matrix} COOC_2H_5 \\ | \\ COOC_2H_5 \end{matrix}} + 2NH_2\cdot NH_2 = \underset{\text{Dihydrazide.}}{\begin{matrix} CO\cdot NH\cdot NH_2 \\ | \\ CO\cdot NH\cdot NH_2 \end{matrix}} + 2C_2H_5OH$$

Esters of Inorganic Acids

In addition to the alkyl halides which have been mentioned earlier in this chapter the esters of the inorganic acids include the nitrites, nitrates, and sulphates.

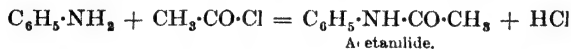
The alkyl nitrites have the general formula R·O·N:O and are esters of nitrous acid. Care must be taken in handling them, as they have a pronounced action on the heart. They may be

detected by means of 2-phenylindole, which gives a precipitate of 3-*iso*nitroso-2-phenylindole.

$$\text{2-phenylindole (}C_6H_5\text{, NH)} \xrightarrow{HNO_2} \text{3-isonitroso-2-phenylindole (=NOH, }C_6H_5\text{, N)}$$

Sulphates such as dimethyl sulphate are identified by the preparation of ethers from suitable phenols. For example, dimethyl sulphate and *sym.*-tribromophenol give a crystalline methyl ether.

$$\text{(OH, Br, Br, Br)} \xrightarrow[NaOH]{(CH_3)_2SO_4} \text{(OCH}_3\text{, Br, Br, Br)}$$

Acid Chlorides

Acid chlorides are very reactive compounds, the aliphatic chlorides, for instance, reacting vigorously with cold water. All acid chlorides react with primary and secondary amines, in many cases in the presence of sodium hydroxide, to give substituted amines, and these are used as derivatives, since they can be easily crystallised and have convenient melting points.

$$C_6H_5{\cdot}NH_2 + CH_3{\cdot}CO{\cdot}Cl = \underset{\text{Acetanilide.}}{C_6H_5{\cdot}NH{\cdot}CO{\cdot}CH_3} + HCl$$

Amides and esters are also obtained by the action of ammonia and alcohols respectively.

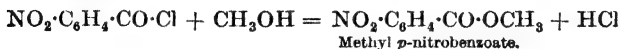
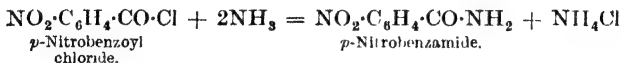
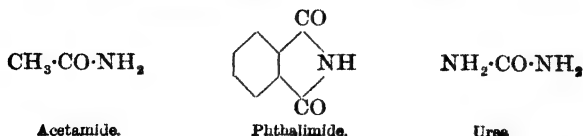
$$\underset{\text{p-Nitrobenzoyl chloride.}}{NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}Cl} + 2NH_3 = \underset{\text{p-Nitrobenzamide.}}{NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}NH_2} + NH_4Cl$$

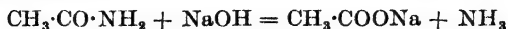
$$NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}Cl + CH_3OH = \underset{\text{Methyl p-nitrobenzoate.}}{NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}OCH_3} + HCl$$

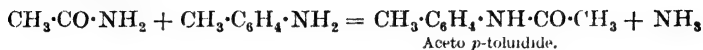
Amides, Imides, and Ureas

$CH_3{\cdot}CO{\cdot}NH_2$ — Acetamide.

$C_6H_4(CO)_2NH$ (CO, NH, CO) — Phthalimide.

$NH_2{\cdot}CO{\cdot}NH_2$ — Urea

Amides and imides yield ammonia on heating with caustic soda, as do the ureas, since these may be regarded as amides of carbonic acid.

$$CH_3 \cdot CO \cdot NH_2 + NaOH = CH_3 \cdot COONa + NH_3$$

p-Toluidides may be prepared by heating the simple amides with *p*-toluidine.

$$CH_3 \cdot CO \cdot NH_2 + CH_3 \cdot C_6H_4 \cdot NH_2 = \underset{\text{Aceto } p\text{-toluidide.}}{CH_3 \cdot C_6H_4 \cdot NH \cdot CO \cdot CH_3} + NH_3$$

On hydrolysis with 50% sulphuric acid the aromatic amides and imides give the corresponding acids, which are identified after crystallisation from water by their melting points.

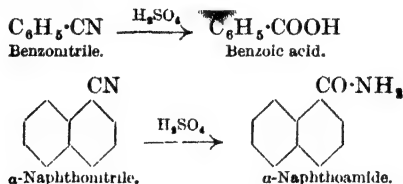
Ureas, after being heated, give the biuret test and form salts such as nitrates and oxalates, which are only slightly soluble in water and have characteristic crystalline forms.

Nitriles

The nitriles differ from ammonium salts and amides in yielding ammonia only on boiling with caustic soda. On boiling the aromatic nitriles with 50% sulphuric acid precipitates of acids or amides are obtained.

$$\underset{\text{Benzonitrile.}}{C_6H_5 \cdot CN} \xrightarrow{H_2SO_4} \underset{\text{Benzoic acid.}}{C_6H_5 \cdot COOH}$$

CN — $\xrightarrow{H_2SO_4}$ — $CO \cdot NH_2$

α-Naphthonitrile. → α-Naphthoamide.

Nitriles can also be identified as addition compounds of mercapto-acetic acid (Condo, Hinkel, Fassero, and Shriner, *J. Amer. Chem. Soc.*, 1937, **59**, 230).

Amines

The amines are substituted ammonias in which one or more hydrogen atoms are replaced by alkyl or aryl groups. They are divided into three classes:

Primary amines which contain the *amino* group $-NH_2$
Secondary amines which contain the *imino* group $>NH$

Tertiary amines in which no hydrogen atoms are attached to the nitrogen atom and which therefore contain the group $>N$.

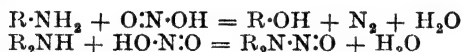
The quaternary ammonium compounds form a fourth closely related group. They have the formula $[NR_4]X$, where X is hydroxyl, halogen, or other acidic radical. These will be considered in a separate section.

Amines, being ammonia derivatives, are bases, the aliphatic compounds being stronger bases than ammonia and the aromatic weaker. They are accordingly soluble in mineral acids: the salts formed with hydrochloric acid can be isolated under suitable conditions and used for identifying amines. They are not always suitable as derivatives, however, as they are sometimes hygroscopic, and their melting points are often not sharp.

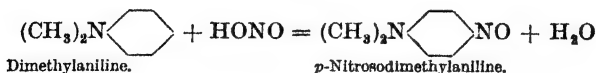
The aliphatic amines have a characteristic ammoniacal, fish-like odour quite different from that of the aromatic amines such as aniline. Aliphatic amines also differ from the aromatic compounds by their solubility in water.

Two reagents are of outstanding value in distinguishing the various types of amines—nitrous acid, and benzenesulphonyl chloride.

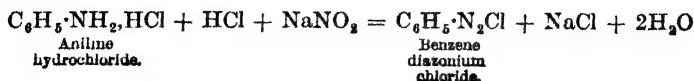
Primary amines in the aliphatic series react with nitrous acid to form alcohols, whereas secondary amines yield nitrosamines in the form of yellow oils or solids.

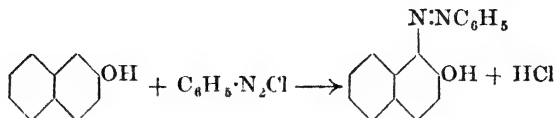
$$R{\cdot}NH_2 + O{:}N{\cdot}OH = R{\cdot}OH + N_2 + H_2O$$
$$R_2NH + HO{\cdot}N{:}O = R_2N{\cdot}N{:}O + H_2O$$

Tertiary amines do not react with nitrous acid except in the case of some aromatic compounds such as *N*:*N*-dimethylaniline, which yields *p*-nitrosodimethylaniline.

$$(CH_3)_2N\langle\bigcirc\rangle + HONO = (CH_3)_2N\langle\bigcirc\rangle NO + H_2O$$

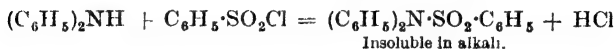
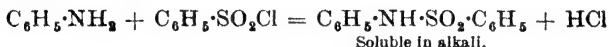
Dimethylaniline. *p*-Nitrosodimethylaniline.

The reaction of the aromatic primary amines towards nitrous acid is characteristic, a solution of a diazonium salt being obtained.

$$C_6H_5{\cdot}NH_2,HCl + HCl + NaNO_2 = C_6H_5{\cdot}N_2Cl + NaCl + 2H_2O$$

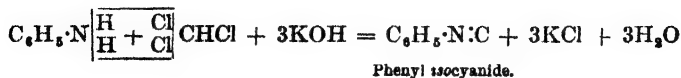
Aniline hydrochloride. Benzene diazonium chloride.

The presence of the diazonium compound is readily shown by adding the solution *to* an alkaline solution of β-naphthol when an intensely coloured precipitate of an azo-compound is obtained. This is the best test for the primary aromatic amines.

$$C_{10}H_7OH + C_6H_5{\cdot}N_2Cl \longrightarrow C_{10}H_6(N{:}NC_6H_5)OH + HCl$$

The benzenesulphonyl chloride test known as Hinsberg's test is also used to classify the amines. The method is based on the fact that benzenesulphonyl chloride reacts with primary and secondary amines but not with the tertiary compounds. The sulphonyl derivatives of the primary amines are distinguished from those of the secondary amines by their solubility in sodium hydroxide solution.

$$C_6H_5{\cdot}NH_2 + C_6H_5{\cdot}SO_2Cl = \underset{\text{Soluble in alkali.}}{C_6H_5{\cdot}NH{\cdot}SO_2{\cdot}C_6H_5} + HCl$$

$$(C_6H_5)_2NH + C_6H_5{\cdot}SO_2Cl = \underset{\text{Insoluble in alkali.}}{(C_6H_5)_2N{\cdot}SO_2{\cdot}C_6H_5} + HCl$$

Primary amines sometimes give disulphonyl derivatives which are also insoluble in alkali, and may therefore lead to the compound being classified incorrectly as a secondary amine. It is advisable for this reason to boil the sulphonamides with sodium ethylate, which converts any disulphonyl derivatives into the monosulphonyl compounds. Weakly basic amines such as *o*-nitraniline form sulphonyl derivatives with difficulty. *p*-Toluenesulphonyl chloride is often used instead of benzenesulphonyl chloride, as it yields compounds with more convenient melting points.

Primary amines may be detected by the sensitive carbylamine test. When heated with alcoholic sodium hydroxide and chloroform they yield *iso*cyanides, which are recognised by their intolerable odour. The test is not given by some amines such as α-naphthylamine.

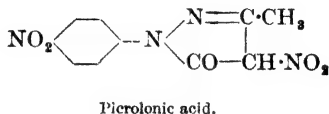
$$C_6H_5{\cdot}N\left|\begin{matrix}H & + & Cl\\ H & + & Cl\end{matrix}\right|CHCl + 3KOH = \underset{\text{Phenyl isocyanide.}}{C_6H_5{\cdot}N{:}C} + 3KCl + 3H_2O$$

Of the many derivatives available for the identification of amines, those of the aromatic series are generally more easily obtained than those of aliphatic character.

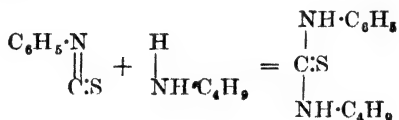
Perhaps the most common reagent is picric acid, which forms picrates with all three types of amines. These derivatives have the drawback, however, that many of them have not sharp melting points, and many of those obtained from the aromatic amines melt at practically the same temperature. The picrates may, therefore, be used with advantage for the detection of amines, but other derivatives should in many cases be used for the final identification. Picric acid in the above reaction may be replaced by other nitro-compounds, the commonest being *sym.*-trinitrobenzene and picrolonic acid.

NO_2, NO_2, NO_2 (benzene ring)

sym.-Trinitrobenzene.

$NO_2 \cdot C_6H_4 - N \langle \begin{matrix} N = C \cdot CH_3 \\ CO - CH \cdot NO_2 \end{matrix}$

Picrolonic acid.

Phenylthioureas, formed by the action of phenyl *iso*thiocyanate on primary and secondary amines, are excellent derivatives both for aliphatic and aromatic amines.

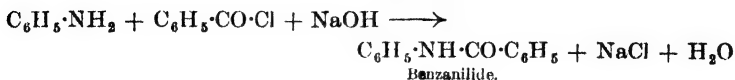
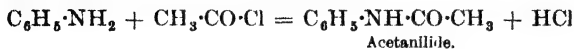
$$\begin{matrix} C_6H_5 \cdot N \\ \| \\ C{:}S \end{matrix} + \begin{matrix} H \\ | \\ NH \cdot C_4H_9 \end{matrix} = \begin{matrix} NH \cdot C_6H_5 \\ | \\ C{:}S \\ | \\ NH \cdot C_4H_9 \end{matrix}$$

Other similar reagents such as 4-diphenylyl and α- and β-naphthyl *iso*thiocyanates have been recommended.

Acetyl and benzoyl compounds of the amines are often used especially in the aromatic series.

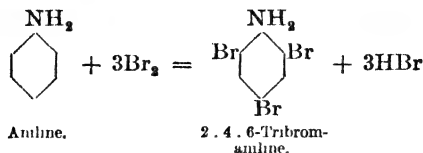
$$C_6H_5 \cdot NH_2 + CH_3 \cdot CO \cdot Cl = C_6H_5 \cdot NH \cdot CO \cdot CH_3 + HCl$$

Acetanilide.

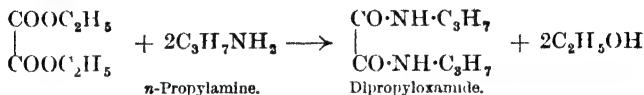
$$C_6H_5 \cdot NH_2 + C_6H_5 \cdot CO \cdot Cl + NaOH \longrightarrow C_6H_5 \cdot NH \cdot CO \cdot C_6H_5 + NaCl + H_2O$$

Benzanilide.

Bromination is used for many aromatic amines, aniline, for instance, being identified by conversion into tribromaniline.

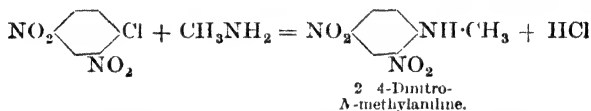
$$C_6H_5NH_2 + 3Br_2 = C_6H_2Br_3NH_2 + 3HBr$$

Aniline. 2 . 4 . 6-Tribromaniline.

Substituted oxamides are useful for the identification of the aliphatic amines, being formed by the action of the latter on ethyl oxalate.

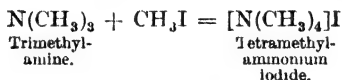
$$\begin{matrix} COOC_2H_5 \\ | \\ COOC_2H_5 \end{matrix} + 2C_3H_7NH_2 \longrightarrow \begin{matrix} CO{\cdot}NH{\cdot}C_3H_7 \\ | \\ CO{\cdot}NH{\cdot}C_3H_7 \end{matrix} + 2C_2H_5OH$$

n-Propylamine. Dipropyloxamide.

1-Chloro-2 : 4-dinitrobenzene gives crystalline derivatives with primary and secondary amines, a condensing reagent such as sodium acetate frequently being necessary.

$$NO_2C_6H_3(NO_2)Cl + CH_3NH_2 = NO_2C_6H_3(NO_2)NH{\cdot}CH_3 + HCl$$

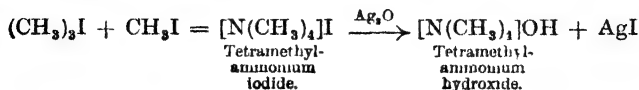
2 4-Dinitro-N-methylaniline.

The identification of the tertiary amines is best effected by means of the quaternary ammonium salts formed by the action of methyl or ethyl iodide.

$$N(CH_3)_3 + CH_3I = [N(CH_3)_4]I$$

Trimethylamine. Tetramethylammonium iodide.

Quaternary Ammonium Compounds

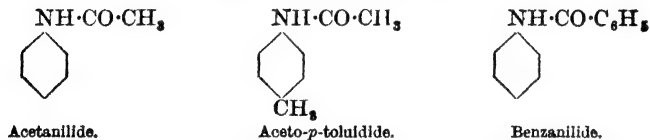
The quaternary salts such as tetramethylammonium iodide, $[N(CH_3)_4]I$, are crystalline solids, soluble in water to give a solution which conducts electricity. They have therefore the properties of salts. They are converted by moist silver oxide into quaternary bases which are strong bases dissolving in water to give strongly alkaline solutions. Many of these are deliquescent.

$$(CH_3)_3I + CH_3I = [N(CH_3)_4]I \xrightarrow{Ag_2O} [N(CH_3)_4]OH + AgI$$

Tetramethylammonium iodide. Tetramethylammonium hydroxide.

Halogeno- and Nitro-Amines

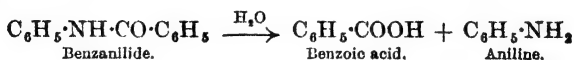
In the substituted amines such as the chloranilines and nitranilines the halogeno- and nitro-groups exert a considerable influence on the properties of the amino group; the basic character, for example, is weakened, and a compound such as *sym.*-tribromaniline does not dissolve in concentrated hydrochloric acid. In certain cases the preparation of derivatives is not so simple as with the unsubstituted amines. In general, however, it is not difficult to detect the presence of the amino group and prepare suitable derivatives.

Substituted Amides

Acetanilide. Aceto-*p*-toluidide. Benzanilide.

The commonest members of this class are the anilides and the toluidides, of which examples are given above. They respond to the Tafel reaction by giving bright colours with concentrated sulphuric acid and potassium dichromate. A few compounds such as *p*-nitracetanilide do not give the test.

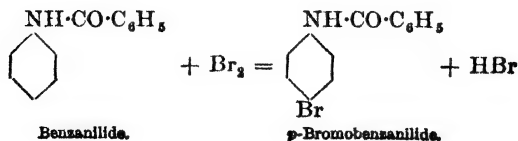
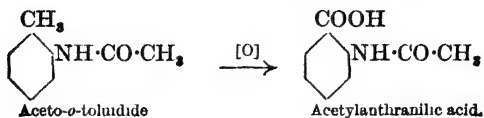
Derivatives are most easily obtained by hydrolysis with 50% sulphuric acid. Many of the acids and amines obtained in this way are crystalline compounds which have definite melting points.

$$C_6H_5\cdot NH\cdot CO\cdot C_6H_5 \xrightarrow{H_2O} C_6H_5\cdot COOH + C_6H_5\cdot NH_2$$

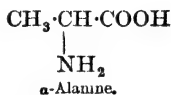
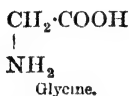
Benzanilide. Benzoic acid. Aniline.

Nitro- and bromo-compounds can often be obtained, and oxidation with potassium permanganate is used when possible, as it is very easily carried out.

$$C_6H_5\cdot NH\cdot CO\cdot C_6H_5 + Br_2 = Br\cdot C_6H_4\cdot NH\cdot CO\cdot C_6H_5 + HBr$$

Benzanilide. *p*-Bromobenzanilide.

$$\underset{\text{Aceto-}o\text{-toluidide}}{C_6H_4(CH_3)\cdot NH\cdot CO\cdot CH_3} \xrightarrow{[O]} \underset{\text{Acetylanthranilic acid.}}{C_6H_4(COOH)\cdot NH\cdot CO\cdot CH_3}$$

Amino Acids

The commonest amino acids are the α-amino acids, in which the carboxyl and amino groups are attached to the same carbon atom.

$$\underset{\text{Glycine.}}{NH_2\cdot CH_2\cdot COOH} \qquad \underset{\alpha\text{-Alanine.}}{CH_3\cdot CH(NH_2)\cdot COOH}$$

In solution these acids exist in the form of *inner salts*, glycine, for example, having the following formula

$$\overset{+}{N}H_3\cdot CH_2\cdot CO\overset{-}{O}$$

Amino acids have therefore the properties of salts. They have high melting points; are soluble in water but insoluble in organic solvents; and their aqueous solutions are neutral to litmus. These physical properties together with their characteristic crystalline forms are used to detect amino acids. It should be noted, however, that the melting points are often not sharp, and depend on the rate of heating.

Many amino acids are optically active.

Various chemical tests are used for detecting amino acids. They form deep blue salts with copper sulphate or acetate. This is best shown by dissolving the amino acid in water and adding one or two drops of copper sulphate solution, when a deep blue colour is at once observed. The α-amino acids give the exceedingly delicate ninhydrin test.

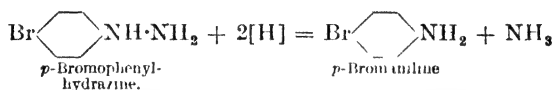
The reagents used for identifying amines are often of value for amino acids. Thus the picrates, and especially the picrolonates, are extensively employed, though they have the disadvantage that their melting points are sometimes not sharp. Recently the *p*-toluenesulphonyl derivatives have been advocated (McChesney and Swann, *J. Amer. Chem. Soc.*, 1937, **59**,

1116). Acetyl and benzoyl derivatives may also be used, but the latter are less readily prepared, owing to the difficulty of removing the benzoic acid formed during the benzoylation. Many amino acids can be identified as their 3 : 5-dinitrobenzoyl derivatives (Saunders, *Biochem. J.*, 1934, **28**, 580).

Hydrazines

The commonest hydrazines are those, such as phenylhydrazine, $C_6H_5 \cdot NH \cdot NH_2$, which belong to the aromatic series and are used extensively in the study of carbohydrates and carbonyl compounds. They are for the most part strongly basic, and form crystalline salts with acids. They reduce Fehling's solution, and on reduction yield amines.

$$Br\langle C_6H_4 \rangle NH \cdot NH_2 + 2[H] = Br\langle C_6H_4 \rangle NH_2 + NH_3$$

p-Bromophenylhydrazine. *p*-Bromaniline

Derivatives are easily obtained by condensing the hydrazines with carbonyl compounds to give hydrazones.

$$(CH_3)_2CO + NH_2 \cdot NH \langle C_6H_3 \rangle (NO_2)_2 = (CH_3)_2C{:}N \cdot NH \langle C_6H_3 \rangle (NO_2)_2 + H_2O$$

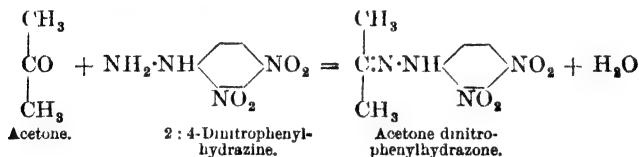
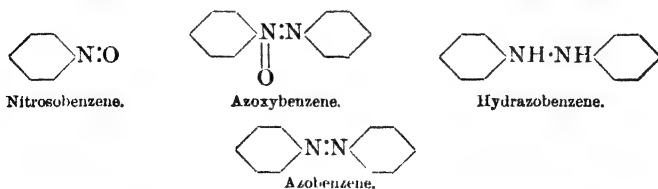
Acetone. 2 : 4-Dinitrophenylhydrazine. Acetone dinitrophenylhydrazone.

Nitroso, Azoxy, Hydrazo, and Azo Compounds

$C_6H_5N{:}O$ — Nitrosobenzene.

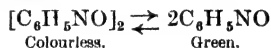
$C_6H_5N(=O){:}NC_6H_5$ — Azoxybenzene.

$C_6H_5NH \cdot NHC_6H_5$ — Hydrazobenzene.

$C_6H_5N{:}NC_6H_5$ — Azobenzene.

In addition to the *C*-nitroso-compounds another class of nitroso-compound is known in which the nitroso group is attached to a nitrogen atom. These nitrosamines will not be dealt with here.

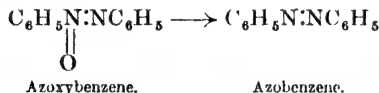
The different types of compounds of which examples are given above have the common property that on reduction with strong reducing reagents they yield amines, and on reduction with zinc dust, calcium chloride, and alcohol they form substituted hydroxylamines. In this respect they resemble the nitro-compounds.

The nitroso-compounds contain the —N=O group, and must not be confused with *iso*nitroso- or oximino-compounds, which contain the =NOH group. They are colourless compounds which on melting or dissolving in organic solvents give intense green or blue colours. This colour change is due to the dissociation of the colourless bimolecular compounds into the coloured monomolecular compounds.

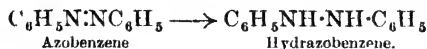
$$\underset{\text{Colourless.}}{[C_6H_5NO]_2} \rightleftarrows \underset{\text{Green.}}{2C_6H_5NO}$$

Many nitroso-compounds give the Liebermann reaction and yield azo derivatives by interaction with primary amines.

$$\underset{\text{Nitroso-benzene.}}{C_6H_5{\cdot}NO} + \underset{\text{Aniline.}}{H_2N{\cdot}C_6H_5} \longrightarrow \underset{\text{Azobenzene.}}{C_6H_5N{:}NC_6H_5} + H_2O$$

The azoxy-compounds are yellow, and on reduction with zinc dust, caustic soda, and alcohol they yield azo or hydrazo derivatives, which are used for identification.

$$\underset{\text{Azoxybenzene.}}{C_6H_5\underset{\underset{O}{\|}}{N}{:}NC_6H_5} \longrightarrow \underset{\text{Azobenzene.}}{C_6H_5N{:}NC_6H_5}$$

The hydrazo-compounds are colourless in the pure state, but readily oxidise in air to coloured azo-compounds.

The azo-compounds are highly coloured, usually orange or red, and on reduction with zinc dust, caustic soda, and alcohol form hydrazo-compounds.

$$\underset{\text{Azobenzene}}{C_6H_5N{:}NC_6H_5} \longrightarrow \underset{\text{Hydrazobenzene.}}{C_6H_5NH{\cdot}NH{\cdot}C_6H_5}$$

Heterocyclic Compounds

Only the heterocyclic bases will be considered—*i.e.*, those compounds which contain nitrogen in the ring. They have often the properties of amines. Thus they form picrates, methiodides,

benzoyl and acetyl derivatives, hydrochlorides, etc. There are, however, many tests peculiar to these heterocyclics—*e.g.*, the pine-splint test for pyrrole and indoles; the formation of indole *iso*nitroso compounds, etc. (see p. 68).

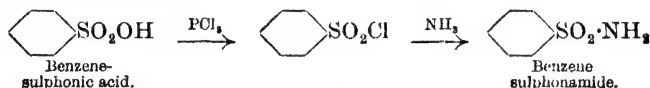
Sulphonic Acids

The sulphur compounds most frequently encountered in the laboratory are the aromatic sulphonic acids and their derivatives. They have the general formula $R{\cdot}S(=O)_2{-}OH$, and, like the carboxylic acids, give rise to derivatives such as the acid chlorides and amides.

The unsubstituted sulphonic acids are liquids or crystalline solids the melting points of which frequently are not sharp. They are difficult to obtain in the pure state, as they are hygroscopic and very soluble in water, but their metallic salts are easily obtained.

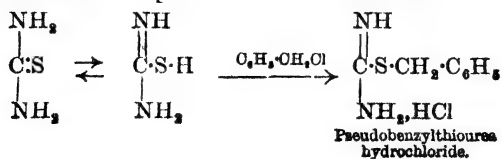
Sulphonic acids are often identified by conversion through the acid chlorides into the amides, which are then purified by crystallisation from water.

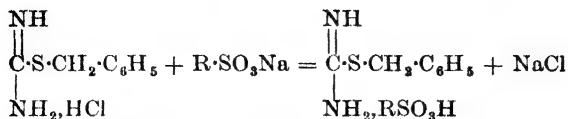
$$C_6H_5SO_2OH \xrightarrow{PCl_5} C_6H_5SO_2Cl \xrightarrow{NH_3} C_6H_5SO_2{\cdot}NH_2$$

Benzene-sulphonic acid. Benzene sulphonamide.

As the acids are strong acids, they may also be identified by their aniline salts. The method is useful, but suffers from the fact that the salts are readily hydrolysed and do not always have sharp and convenient melting points.

A more satisfactory method of identification is the formation of their salts of pseudobenzylthiourea—a method which is also used for the carboxylic acids. The reaction is ionic, and therefore instantaneous. The reagent is formed by the action of benzyl chloride on the pseudo form of thiourea:

$$NH_2{-}C(:S){-}NH_2 \rightleftarrows NH{=}C(SH){-}NH_2 \xrightarrow{C_6H_5{\cdot}CH_2Cl} NH{=}C(S{\cdot}CH_2{\cdot}C_6H_5){-}NH_2,HCl$$

Pseudobenzylthiourea hydrochloride.

Formation of the salts takes place as follows:

$$\begin{array}{l}NH\\ \| \\ C\text{·}S\text{·}CH_2\text{·}C_6H_5\\ | \\ NH_2,HCl\end{array} + R\text{·}SO_3Na = \begin{array}{l}NH\\ \| \\ C\text{·}S\text{·}CH_2\text{·}C_6H_5\\ | \\ NH_2,RSO_3H\end{array} + NaCl$$

Substituted Sulphonic Acids

The most important of these acids are the hydroxylic and amino compounds, many of which are of importance in the dye industry. They can be detected by the characteristic reactions of these groups, many of the hydroxy-sulphonic acids, for example, giving colorations with ferric chloride.

The aminosulphonic acids decompose at high temperatures without melting, and differ from the simple sulphonic acids in their insolubility in water. They readily undergo diazotisation.

Sulphonyl Chlorides

The sulphonyl chlorides are liquids or solids with relatively low melting points. They have an unpleasant clinging odour, and are acted on slowly by water. They are identified by conversion into sulphonamides or sulphonanilides.

Sulphonamides

The sulphonamides are soluble in sodium hydroxide solution giving comparatively stable sodium salts of the formula $R\text{·}SO_2\text{·}NHNa$ which react readily with benzyl chloride to give the *N*-benzyl derivatives.

$$R\text{·}SO_2\text{·}NHNa + C_6H_5\text{·}CH_2\text{·}Cl = R\text{·}SO_2\text{·}NH\text{·}CH_2\text{·}C_6H_5 + NaCl$$

These are the best derivatives for identification.

*Iso*thiocyanates. Thioureas

The *iso*thiocyanates, also known as the mustard oils, have the formula R·N:C:S. They are colourless oils or crystalline solids. They react with amines to form substituted thioureas,

and this reaction is used for the identification both of amines and of *iso*thiocyanates (see p. 72).

The thioureas are crystalline solids which on treatment with hydrochloric acid or acetic anhydride yield mustard oils. Many of the disubstituted thioureas, such as diphenylthiourea, are of importance. Various derivatives, such as picrates, acetyl derivatives, etc., can be made.

CHAPTER V

PREPARATION OF DERIVATIVES

THE final stage in the identification of a compound is the preparation of crystalline derivatives and determination of their melting points. The following is an example of the method taken from the literature :

p-Bromonitrosobenzene — $NO{\cdot}C_6H_4{\cdot}Br$

was identified by its melting point, by a mixed melting point with a specimen prepared by oxidation of *p*-bromaniline, and by analysis. To make quite sure of its identity, it was condensed with a molecular proportion of aniline, and the *p*-bromoazobenzene produced (m.p. 89°, orange leaflets from dilute acetic acid) identified with a specimen prepared in like manner from *p*-bromaniline and nitrosobenzene (Ingold, *J.*, 1925, **127**, 516).

For a given class of compound there are generally several reagents available for the preparation of derivatives, and the choice of reagent is not always easy. Thus for carbonyl compounds 2 : 4-dinitrophenylhydrazine is extremely suitable : on the other hand, for aromatic hydrocarbons a choice has to be made between bromination, nitration, oxidation, and molecular compound formation. The following rules regarding the suitability of reagents are often of use in making the final selection (cf. *Rec. trav. chim.*, 1935, **54**, 517).

Identification Reagents.

1. Must be easily obtained.
2. Must be stable under ordinary conditions.
3. Must react rapidly with the compound to be identified.
4. Must yield compounds which can be readily isolated and purified.
5. The melting points of the resulting compounds should lie between 80° and 250°, and should be sharp.

6. The melting points of the derivatives of adjacent homologues should differ by at least ten degrees.

The application of these rules may be illustrated by a consideration of carbonyl reagents, of which the chief are dinitrophenylhydrazine, phenylhydrazine, hydroxylamine hydrochloride, and semicarbazide hydrochloride. Dinitrophenylhydrazine is prepared extremely easily, and is quite stable. It reacts in a few seconds with carbonyl compounds, yielding dinitrophenylhydrazones, which are crystalline compounds easily purified by crystallisation. The melting points of the dinitrophenylhydrazones are sharp, and mostly lie between 100° and 250°. Each of the other reagents has some disadvantage. Some of the simple phenylhydrazones, such as acetone phenylhydrazone, are oils. The oximes are not always easily prepared, while the semicarbazones not only have the disadvantage that they may take many hours to prepare, but also their melting points frequently vary with the rate of heating. Dinitrophenylhydrazine is therefore obviously first choice as a reagent for carbonyl compounds.

In this chapter details are given for the preparation and purification of derivatives. Chapter IV is intended to help in the choice of derivatives for different classes of compounds, while Part B describes the properties of some of the more important organic compounds and their derivatives. The derivatives given are suitable for the identification of small quantities of substances. With a few exceptions 0·5 g. of a compound is sufficient, and in many cases 0·1 g. is ample. The handling of such small quantities is at first somewhat difficult to the student accustomed to the preparation of organic compounds on the large scale, but with a little practice and assistance the necessary technique is soon acquired. The preparations are carried out in test-tubes, and only in a few cases are small flasks necessary. The methods of purification given on pp. 15–19 should be studied.

Derivatives

1. Bromo Derivatives

The compound is dissolved or suspended in glacial acetic acid, and a solution of bromine in acetic acid is added until the colour

of bromine persists. The liquid is gently warmed, more bromine is added if it loses its brown colour, and the mixture is allowed to stand at room temperature for some time—generally about 15 minutes. If no precipitate separates, water is added drop by drop until crystals appear. The bromo-compound thus obtained is filtered, washed with dilute sodium carbonate solution and then with water, and finally crystallised from alcohol.

Carbon tetrachloride or chloroform is often used as solvent instead of acetic acid. In this case if no crystals separate the solvent is removed by evaporation until crystals appear.

2. Nitro Derivatives

There is no method of nitration applicable to all aromatic compounds. Four of the most useful are given.

(*a*) About 0·2 g. of the compound is added to a mixture of 2 c.c. concentrated sulphuric and 2 c.c. concentrated nitric acid. The mixture is well shaken, heated for 30 seconds, and is then poured into 10 c.c. water. On cooling, the oily suspension yields a solid which is collected in a filter, washed with cold water, and recrystallised from alcohol or aqueous alcohol.

(*b*) As in (*a*), except that fuming nitric acid (d, 1·5) is used instead of concentrated nitric acid (d, 1·42).

(*c*) About 0·5 g. of the compound is boiled with 4 c.c. of fuming nitric acid. The length of the time necessary for heating varies with the compound, but should not exceed 30 minutes. The nitro-compound is obtained as a solid on pouring the solution into water (10 c.c.), and is purified by washing with water and crystallisation from alcohol or aqueous alcohol.

(*d*) The compound (0·3 g.) is dissolved in glacial acetic acid (4 c.c.), fuming HNO_3 (3 c.c.) is carefully added, and the mixture heated to boiling. After standing for 10 minutes the solution is poured into water (10 c.c.). On cooling and shaking, a precipitate is formed which after washing with water is crystallised from alcohol or aqueous alcohol.

3. Oxidation to Carboxylic Acids

The oxidation of side-chains is so dependent on factors such as the nature of the side-chain and the oxidising agent employed

that it is difficult to give a method of general application. The following procedure is often used. 1 G. of the compound, 2 g. potassium permanganate (finely powdered), and 50 c.c. water are heated over a small flame until the colour of the permanganate has disappeared, or for 3 hours. If violent bumping occurs, the flask should be immersed in a bath of boiling water and heated by this means. When oxidation is complete the hot solution is filtered and the filtrate acidified with sulphurous acid. The solution on cooling deposits the acid, which is purified by crystallisation from boiling water or from aqueous alcohol. The melting points of some of the aromatic acids are too high to be of use. In such cases the acids may be converted into their methyl esters, which have definite readily determined melting points.

4. Oxidation to Quinones

Chromic acid (1 g.) is dissolved in 2 c.c. water and added to a suspension or solution of the hydrocarbon (0·5 g.) in 10 c.c. acetic acid, and the mixture heated gently by a small flame for 2 minutes. If the reaction becomes too violent the test-tube is cooled in running water. The solution is allowed to stand for ¼ hour. If the quinone does not separate out water is added until crystallisation occurs. The quinones are purified by crystallisation from glacial acetic acid or by sublimation.

5. Molecular Compounds. Picrates, etc.

The method given for the preparation of molecular compounds is applicable not only to the preparation of the picrates, but also of other compounds such as the picrolonates, *sym.*-trinitrobenzene derivatives, etc.

The compound is dissolved in the *minimum* amount of boiling alcohol, and is added to a similar solution containing a little more than the same weight of picric acid. The solution is cooled and the picrate separates out. The picrates are readily crystallised from alcohol, but, in the case of some which are unstable, alcohol saturated with picric acid is necessary. In some cases it is better to use benzene as a solvent for the preparation of picrates, as some of the latter are unstable in presence of a little water. It is advisable to make only small quantities of picrates,

and to heat a minute quantity on a spatula before determining the melting point, as a few of them are explosive.

6. Alkylisothiourea Picrates

Finely powdered thiourea (1 g.), alkyl halide (1 g.), and alcohol (10 c.c.) are boiled under reflux for 5 minutes or longer, depending on the nature of the halide. Picric acid (1 g.) is then added, and the mixture heated until a clear solution is obtained. The solution on cooling or on the addition of a little water deposits the picrate, which is purified by crystallisation from alcohol.

7. Reduction

(*a*) *To Amines.* The nitro-compound (1 g.) is suspended in concentrated hydrochloric acid (10 c.c.) and alcohol (2 c.c.) is added. Several pieces of tin are then added, and a brisk reaction sets in when the mixture is gently heated. When a clear solution is obtained it is decanted from any unused tin. On the addition of 30% sodium hydroxide solution until the tin hydroxide first formed is dissolved the amine separates, generally as an oil. The mixture is extracted with 20 c.c. of ether, and the ether extract evaporated on the water-bath. The amine so obtained is identified by means of its acetyl or benzoyl derivative.

(*b*) *To Hydrazo- and Azo-Compounds.* The compound (1 g.), alcohol (10 c.c.), sodium hydroxide (1 g.), and zinc dust (2 g.) are refluxed for 20 minutes and the mixture is filtered while hot. The filtrate on cooling deposits the hydrazo- or azo-compound in the pure state.

8. Esters

(*a*) *From Acids.* About 0·4 g. of the acid is dissolved in 5 c.c. of the alcohol, and five drops of concentrated sulphuric acid are added. In cases where the acid is only slightly soluble in alcohol double this quantity of alcohol should be used. The solution is gently heated for 30 minutes in a small flask provided with a 4-feet piece of glass tubing as condenser. A crystalline precipitate of the ester is obtained by cooling the solution or by the addition of a few drops of water, and is crystallised from alcohol.

Solid esters are obtained only from a limited number of acids, such as *p*-nitrobenzoic and 3 : 5-dinitrobenzoic acids.

(*b*) *From Acid Chlorides.* The acid (0·5 g.) is converted into the acid chloride as in the preparation of the amides (p. 89). The alcohol (1 c.c.) is then added and is gently heated above a small flame for 2 minutes. Water (5 c.c.) and sodium carbonate solution (5 c.c.) are added, and the resulting solid, after being washed with water, is crystallised either from alcohol or, in the case of low-melting compounds, from petrol ether (40—60°).

9. Benzoylation

(*a*) About 0·3 g. of the compound is heated with 0·5 c.c. benzoyl chloride and 10 c.c. 10% sodium hydroxide solution until the smell of benzoyl chloride has disappeared. The solution must still be alkaline at this stage (test with litmus). It is then cooled and shaken until a precipitate appears. The benzoyl compound is separated, washed with water, and recrystallised from alcohol.

(*b*) A second method is frequently used. Equimolecular quantities of the compound and benzoyl chloride are dissolved in pyridine, and the solution is allowed to stand overnight. The benzoyl compound is obtained in good yield on diluting the solution with water. It is washed first with dilute hydrochloric acid to remove pyridine, then with sodium carbonate solution to remove any benzoic acid formed, and finally with water. It is crystallised from alcohol.

10. Acetylation

Approximately 0·3 g. of the compound is boiled with 0·5 c.c. acetic anhydride containing a trace of concentrated sulphuric acid (1 c.c. of acetic anhydride to one drop of sulphuric acid). After a minute water is added drop by drop. The turbid mixture generally gives a precipitate of the acetyl compound on shaking. If an oily product is obtained it should be gently heated with sodium bicarbonate solution to remove any adhering acetic acid. A solid is thus obtained which is crystallised from boiling water or alcohol.

11. Aryloxyacetic Acids

The preparation of these acids has been worked out by Koelsch (*J.A.C.S.*, 1931, **53**, 304). About 1 g. of the phenol, 3·5 c.c.

caustic soda solution (30%), and 2·5 c.c. 50% aqueous monochloracetic acid are shaken together, and if necessary 5 c.c. water added to dissolve the sodium salt of the phenol. The solution is placed in a test-tube and heated in a boiling water-bath for 1 hour. It is then cooled, diluted with 10 c.c. of water, and dilute HCl added until the mixture is acid to Congo Red indicator. The mixture is immediately extracted with ether, the ether extract washed once with water and then shaken with 20 c.c. of sodium carbonate solution. The sodium carbonate layer is next acidified with dilute hydrochloric acid. The resultant aryloxyacetic acid is separated and recrystallised from water or aqueous alcohol. The method is satisfactory with small quantities of phenols, but is not applicable to nitrophenols.

12. Phenylhydrazones

Equal quantities (about five drops) of the carbonyl compound and phenylhydrazine are heated over a small flame for 2 minutes. Alcohol (1 c.c.) is added, and then water drop by drop until crystallisation occurs. The precipitate is recrystallised from alcohol.

13. 2 : 4-Dinitrophenylhydrazones

Two methods are available.

(*a*) *Allen's Method.* The stock solution (see Appendix) is well shaken and 5 c.c. of the solution containing the dinitrophenyl hydrazine in suspension are added to 5 c.c. of alcohol containing a few drops of the carbonyl compound. The solution is heated to the boiling point and two or three drops of concentrated hydrochloric acid are then added. The solution is boiled for 30 seconds and cooled. If no precipitate is obtained, water is added until crystals appear. The precipitate is crystallised from alcohol or, in the case of the dinitrophenylhydrazones of aromatic compounds, from glacial acetic acid or tetralin.

(*b*) ***Brady's Method.*** 2 : 4-Dinitrophenylhydrazine (1 g.) is dissolved in concentrated sulphuric acid (2 c.c.) and alcohol (15 c.c.) is added. The carbonyl compound (1/200 mol.) in alcohol is added to the solution. In some cases the dinitrophenylhydrazones separate out immediately: in other cases it may

be necessary to add dilute sulphuric acid before crystallisation sets in. The precipitate is crystallised from alcohol or glacial acetic acid.

14. Semicarbazones

(*a*) *Compounds Soluble in Water.* About 0·5 g. of semicarbazide hydrochloride is dissolved in a saturated solution of sodium acetate (2 c.c.). 0·5 G. of the carbonyl compound is added, and the solution is well shaken. The crystalline semicarbazone generally separates out in a short time. It is separated, washed with 3 c.c. of water, and crystallised from methyl alcohol.

(*b*) *Compounds Insoluble in Water.* As above, except that methyl alcohol (3 c.c.) is added to the solution. If the semicarbazone separates out, it is filtered and crystallised—many of the aromatic semicarbazones are best crystallised from acetic acid. If no crystalline semicarbazone separates, methyl alcohol is added until a clear solution is formed, and the solution is allowed to stand over-night. A crystalline mass is obtained: in some cases it is necessary to add water to cause precipitation.

The melting points of many semicarbazones are dependent on the rate of heating, and frequently are not sharp.

15. Quinoxalines

Equal quantities of the di-carbonyl compound and an *ortho* diamino compound—*o*-phenylenediamine is commonly used—are each dissolved in the minimum quantity of boiling acetic acid, and the solutions mixed. A precipitate of the quinoxaline is obtained by cooling the solution or by the addition of water. It is crystallised from acetic acid.

16. Osazones

The sugar (0·2 g.), phenylhydrazine hydrochloride (0·4 g.), and crystalline sodium acetate (0·6 g.) are shaken with distilled water (4 c.c.), and the solution is filtered from any tarry matter. The test-tube is plugged with cotton wool and placed in a beaker of boiling water. It is occasionally shaken. The time necessary for the precipitation of the osazone is noted, and is characteristic for each sugar. The osazones have fairly definite melting points, and their appearance under the microscope is characteristic.

Time Required for Osazone Formation.

d-Mannose	0·5 minutes (phenylhydrazone).
d-Fructose	2 minutes.
d-Glucose	5 minutes.
l-Rhamnose	7 minutes.
l-Arabinose	10 minutes (oily).
d-Galactose	15–19 minutes.
Sucrose	30 minutes.
Raffinose	60 minutes.
Lactose	No precipitate from hot solution.
Maltose	No precipitate from hot solution.

17. Amides

(*a*) *From Acids.* The acid (1 g.) and phosphorus pentachloride (1 g.)—excess phosphorus pentachloride must be avoided—are heated over a small flame for 30 seconds, and the solution is cooled. Conc. ammonia (5 c.c.) is added drop by drop from a pipette. If the amide separates in lumps, these should be powdered by means of a glass rod. Water is then added, and the amide separated. It is crystallised from hot water, or in some cases from alcohol.

(*b*) *From Esters and Anhydrides.* The ester (0·5 g.) or anhydride is shaken with 10 c.c. concentrated ammonia in a small, glass-stoppered bottle until a solid is obtained. Generally a few minutes are sufficient. The solid amide is filtered, washed with water, and recrystallised from water or alcohol.

18. *p*-Toluidides

1 Part of the acid or anhydride and five parts of *p*-toluidine are heated in an oil-bath at 220° for 20 minutes. The mixture is cooled, and digested with dilute hydrochloric acid. The precipitate is washed with water and dilute alcohol, and crystallised from glacial acetic acid.

19. Aniline Salts

(*a*) The acid (0·4 g.) is dissolved in the minimum quantity of boiling water, and a few drops of aniline are added. On cooling

the solution in ice, a crystalline mass is obtained, which after being dried on porous plate is recrystallised from benzene.

(*b*) *For Sulphonic Acids.* The acid is dissolved in boiling absolute alcohol or preferably in dioxan. A few drops of aniline are added, and on treating the solution as in (*a*) the aniline salt is obtained. It is purified by washing with absolute alcohol.

20. Phenylhydrazides

Equal quantities of the acid and phenylhydrazine are heated in a test-tube *above* a small flame until a clear solution is obtained. The test-tube is then placed in a beaker of boiling water for an hour. On cooling, a solid or semi-solid mass is obtained which on crystallisation from alcohol gives the pure phenylhydrazide.

21. 2-Alkylbenziminazole Picrates

o-Phenylenediamine (0·5 g.), acid (0·5 g.), and 4 c.c. 4N–HCl are refluxed for 15 minutes. The solution is then cooled, and concentrated ammonia added until the alkylbenziminazole separates. This is filtered, and washed well with water. It is dissolved in the minimum quantity of boiling alcohol and added to 0·5 g. picric acid dissolved in the minimum quantity of boiling alcohol. The solution on cooling deposits the picrate, which is purified by crystallisation from alcohol.

22. Anilic Acids

A small amount of the anhydride is dissolved in chloroform or benzene and a few drops of aniline are added. The anilic acid separates immediately, and is recrystallised from acetone.

23. *p*-Nitrobenzyl Esters

The acid (1 g.) is added to 5 c.c. of water and neutralised with 10% caustic soda solution (phenolphthalein). Two or three drops of dilute hydrochloric acid are then added so that the solution is slightly acid. This solution is added to a solution of *p*-nitrobenzyl bromide (1 g.) in alcohol (20 c.c.), and the mixture boiled for an hour: if the acid is dibasic it is boiled for 2 hours. The solution is then allowed to cool, and the ester separates in the crystalline state. It is purified by crystallisation from alcohol

24. Hydrazides

The ester (0·5 c.c.) is dissolved in alcohol and treated with 50% hydrazine hydrate solution (0·5 c.c.). If the hydrazide does not separate immediately, the solution is allowed to stand over-night at room temperature. In some cases separation only occurs after two or three days.

25. Hydrolysis

(*a*) *Esters.* The ester (1 g.) is refluxed for 30 minutes with 10% caustic soda (10 c.c.) and alcohol (10 c.c.). The acid, if it is aromatic, separates on acidification with dilute hydrochloric acid, and is recrystallised from water or aqueous alcohol.

(*b*) *Amides, Anilides, etc.* The amide (1 g.) is refluxed for 30 minutes with 50% sulphuric acid (10 c.c.), and after cooling the solution it is poured into water. Aromatic acids separate, and are crystallised from water or aqueous alcohol.

(*c*) *Nitriles.* Nitriles may be hydrolysed by the method given for amides. They may also be hydrolysed by use of alcoholic potassium hydroxide, in which case the products are often the amides, and not the corresponding acids. The nitrile (1 g.) is dissolved in 10 c.c. saturated alcoholic potassium hydroxide solution and refluxed for 45 minutes. On acidification with hydrochloric acid, the acid or amide is obtained, and is recrystallised from water or aqueous alcohol.

For amides and nitriles which are hydrolysed with difficulty the method of Goldstein and Matthey (*Helv.*, 1937, **20**, 1418), using sulphuric acid, acetic acid, and water, is useful.

26. Hydrochlorides of Bases

Several drops of the base are added to dry benzene (5 c.c.), and dry HCl gas is passed through the solution until a copious precipitate of the hydrochloride is formed. The hydrochloride thus formed is generally pure, but it may be crystallised from a mixture of alcohol and benzene, or by dissolving the hydrochloride in boiling alcohol, adding ether until the solution is slightly turbid, and then cooling the solution.

27. Benzene- and *p*-Toluene-sulphonyl Derivatives

These may be made by the method given on p. 42. For certain amines and for amino-acids the following method is more satisfactory (McChesney and Swann, *J. Amer. Chem. Soc.*, 1937, **59**, 1116). The amino acid (1 g. for aliphatic acids, 2 g. for aromatic acids) is dissolved in 20 c.c. of N sodium hydroxide and added to *p*-toluenesulphonyl chloride (2 g.) in ether (15 c.c.). The solution is shaken for 1 hour, and the ether layer removed. The aqueous solution is acidified with hydrochloric acid to Congo Red. The sulphonyl derivative begins to crystallise at once, or an oil separates which solidifies on standing in the cold. The compound is crystallised from 50% aqueous alcohol.

28. Phenylthioureas

Equal quantities of the amine and phenyl *iso*thiocyanate are mixed, and if no spontaneous reaction occurs, the mixture is gently heated for 2 minutes. Aqueous alcohol is added, and the solution on cooling deposits the thiourea, which is then crystallised from alcohol.

29. Substituted Oxamides

Equal quantities of the amine and ethyl oxalate are gently heated for two minutes and water is then added. The precipitate formed is washed with water, and recrystallised from alcohol.

30. 2 : 4-Dinitrophenyl Derivatives

A saturated solution of 1-chloro-2 : 4-dinitrobenzene is added to alcohol containing a few drops of the amine. The dinitro-compound soon begins to separate. After five minutes it is collected on a filter and recrystallised from alcohol.

In many cases it is necessary to add sodium acetate as a condensing agent.

31. Quaternary Ammonium Salts

The tertiary amine (0·5 g.) and methyl iodide (0·5 g.) are warmed *above* a small flame for two minutes, and then cooled in the ice-bath. If no crystals separate, the side of the test-tube is scratched with the jagged end of a glass rod to induce crystallisation. The

product is crystallised from absolute alcohol after being washed with a little ether.

Some of the quaternary salts are prepared by using ether as a solvent, but in such cases it is often necessary to leave the solution standing over-night. The pure compound is thus obtained directly.

32. Pseudobenzylthiourea Salts

Pseudobenzylthiourea hydrochloride is readily prepared from benzyl chloride and thiourea by the method used by Donleavy (*J. Amer. Chem. Soc.*, 1936, **58**, 1004). The acid (1 g.) to be identified is neutralised by adding aqueous sodium hydroxide from a burette. This solution is then added to a slight excess of pseudobenzylthiourea hydrochloride dissolved in a small amount of boiling alcohol. The product obtained on cooling is purified if necessary by crystallisation from alcohol.

References

References are here given to recent original papers dealing with the preparation of derivatives for identification purposes. Some of the methods are given in this book.

Hydrocarbons

Arylbenzoic acids. Underwood and Walsh, *J. Amer. Chem. Soc.*, 1935, **57**, 940.
Picrates. Baril and Hauber, *J. Amer. Chem. Soc.*, 1931, **53**, 1087.
Acetamido compounds. Ipatieff and Scherling, *J. Amer. Chem. Soc.*, 1937, **59**, 1057.
Oxidation to substituted benzoic acids. Campbell, Brown, and Learmonth, *J. Chem. Educ.*, 1938, **15**, 217.

Alkyl Halides

N-Alkyl-*p*-bromobenzenesulphon-*p*-anisides. Gillespie, *J. Amer. Chem. Soc.*, 1934, **56**, 2740.
Alkyl*iso*thiourea picrates. Brown and Campbell, *J.*, 1937, 1699.

Alcohols

α-Naphthylurethanes. Bickel and French, *J. Amer. Chem. Soc.*, 1926, **48**, 747. French and Wirtel, *J. Amer. Chem. Soc.*, 1926, **48**, 1736.
Diphenylurethanes. Morgan and Pettet, *J.*, 1931, 1124.
p-Nitrobenzoates. Henstock, *J.*, 1933, 216. Adamson and Kenner, *J.*, 1935, 287. Buchner and Meisenheimer, *Ber.*, 1905, **38**, 624. Reichstein, *Helv. Chim. Acta*, 1926, **9**, 799.

Phenols

α-Naphthylurethanes. French and Wirtel, *J. Amer. Chem. Soc.*, 1926, **48**, 1736.
p-Nitrobenzyl ethers. Reid and Lyman, *J. Amer. Chem. Soc.*, 1920, **42**, 615.
Aryloxyacetic acids. Koelsch, *J. Amer. Chem. Soc.*, 1931, **53**, 304.
2 : 4-Dinitrophenyl ethers. Bost and Nicholson, *J. Amer. Chem. Soc.*, 1935, **57**, 2368.

Aldehydes and Ketones

Dinitrophenylhydrazones. Brady, *Analyst*, 1926, **51**, 77. Brady, *J.*, 1931, 756. Allen, *J. Amer. Chem. Soc.*, 1930, **52**, 2955. Strain, *J. Amer. Chem. Soc.*, 1935, **57**, 758. Campbell, *Analyst*, 1936, **61**, 391. Allen and Richmond, *J. Org. Chem.*, 1937, **2**, 222.
Oximes. Lapworth and Steele, *J.*, 1911, **99**, 1884.
Nitrobenzenesulphonhydrazones. Cameron and Storrie, *J.*, 1934, 1330.
Aldimethones. Klein and Lindser, *Mikrochem.*, 1929 (Pregl-Festschrift), 205.

Carboxylic Acids

Amine salts. Buehler, Carson, and Edds, *J. Amer. Chem. Soc.*, 1935, **57**, 2180.
Piperazine salts. Pollard, Adelson, and Bain, *J. Amer. Chem. Soc.*, 1934, **56**, 1759.
p-Nitrobenzyl esters. Reid and co-workers, *J. Amer. Chem. Soc.*, 1917, **39**, 1727, etc.
Anilides. Kuehn and McElvain, *J. Amer. Chem. Soc.*, 1931, **53**, 1173. Robertson, *J.*, 1919, **115**, 1210.
Pseudobenzylthiourea salts. Donleavy, *J. Amer. Chem. Soc.*, 1936, **58**, 1004.
Benziminazole picrates. Brown and Campbell, *J.*, 1937, 1699.
Benziminazoles. Pool, Harwood, and Ralston, *J. Amer. Chem. Soc.*, 1937, **59**, 178.
p-Phenylphenacyl esters. Drake and Bronitsky, *J. Amer. Chem. Soc.*, 1930, **52**, 3715. Drake and Sweeney, *J. Amer. Chem. Soc.*, 1932, **54**, 2059.

Amino Acids

p-Toluenesulphonyl derivatives. McChesney and Swann, *J. Amer. Chem. Soc.*, 1937, **59**, 1116.
Dinitrobenzoyl derivatives. Saunders, *Biochem. J.*, 1934, **28**, 580.

Esters

Anilides. Hardy, *J.*, 1936, 398.
N-Benzylamides. Buehler and Mackenzie, *J. Amer. Chem. Soc.*, 1937, **59**, 421.
p-Toluidides. Koelsch and Tenenbaum, *J. Amer. Chem. Soc.*, 1933, **55**, 3049.
Hydrolysis. Redemann and Lucas, *Ind. Eng. Chem. (Anal.)*, 1937, **9**, 521.

Nitriles

3-Oximino-2-phenylindole. Brown and Campbell, *J.*, 1937, 1699.

Nitriles

Addition compounds of mercapto-acetic acid. Condo, Hinkel, Fassero, and Shriner, *J. Amer. Chem. Soc.*, 1937, **59**, 230.

Amines

2-Nitro-indanion salts. Wanag and Lode, *Ber.*, 1937, **70**, 547.
α-Naphthylthioureas. Suter and Moffett, *J. Amer. Chem. Soc.*, 1933, **55**, 2497.
Phenyl and tolylthioureas. Whitmore and Otterbacher, *J. Amer. Chem. Soc.*, 1929, **51**, 1909.
β-Naphthyl and diphenylylthioureas. Brown and Campbell, *J.*, 1937, 1699.
Salts of 3 : 5-dinitrobenzoic acid. Buehler, Wood, Laurence, *Ind. Eng. Chem. (Anal.)*, 1933, **5**, 277.
Sulphonanilides. Young, *J. Amer. Chem. Soc.*, 1934, **56**, 2167, 2783; 1935, **57**, 773.
m-Nitrobenzenesulphonamides. Marvel, Kingsbury, and Smith, *J. Amer. Chem. Soc.*, 1925, **47**, 166.
2 : 4-Dinitrobenzal derivatives. Lowy, *J. Amer. Chem. Soc.*, 1920, **42**, 849; 1921, **43**, 346; 1923, **45**, 1060. Bennett, *J.*, 1929, 1465.
Quaternary salts. Marvel, Scott, and Amstutz, *J. Amer. Chem. Soc.*, 1929, **51**, 3638.

Sulphonic Acids

p-Toluidine salts. Fieser, *Organic Syntheses*, Vol. 16, p. 65.
Phenylhydrazine salts. Latimer and Bost, *J. Amer. Chem. Soc.*, 1937, **59**, 2500.

CHAPTER VI

EXAMINATION OF MIXTURES

MIXTURES of compounds are commonly encountered in organic chemistry, and are generally recognised by microscopic inspection or by the wide range over which they melt or boil. A systematic examination of such mixtures is usually impossible until they have been separated into their components. This chapter deals with such separations, and, for the sake of simplicity, mixtures of only two components will be considered. The compounds isolated are purified and identified by the methods described in earlier chapters.

The separation of mixtures is frequently a difficult task demanding skill and experience, especially when only small quantities of material are available. The task is somewhat lightened when, as happens occasionally in research, some indication of the nature of the mixture is obtained from the method by which it has been isolated. To take a simple example: in the bromination of benzene the formation of bromobenzene is accompanied by that of *p*-dibromobenzene. The liquid bromobenzene is considerably more volatile in steam than the solid dibromo-compound, and this affords an easy method for their separation. In general, separations are effected by making use of differences of chemical or physical properties of the components of the mixture.

It is not easy to give any fixed procedure for effecting separations, but the following instructions are of wide application.

Before attempting the separation some preliminary tests should be applied to the mixture.

Ignition test.

Elements test.

Physical appearance. Colour, etc. In the case of solids, microscopic examination.

Solubility in caustic soda, dil. hydrochloric acid, water, alcohol, ether, etc.

Ferric chloride test.

Litmus test.

In this way evidence may be obtained as to the nature of one or both of the components, and the best method of separation. Thus, if a basic substance is present, it will be removed by dilute hydrochloric acid. Again, if a mixture otherwise not readily soluble in water dissolves in sodium hydroxide solution and the ferric chloride test indicates the presence of a phenol, it is either a mixture of phenols or a mixture of an acid and phenol. The second alternative suggests separation by means of sodium bicarbonate (see below).

In separating mixtures the main rule to be observed is that the method used must not be too drastic. For instance, distillation of liquids should not be attempted until it is shown that neither component is destroyed by heat. This may be shown by heating a small quantity of the mixture in a test-tube over a small flame and observing if any decomposition sets in. Similarly, sublimation should not be tried until a small-scale test shows that it takes place without any appreciable decomposition.

Various kinds of mixtures are encountered. Each will be considered separately.

(1) **Two Liquids.** Immiscible liquids are, of course, easily separated by means of a separating-funnel. In other cases the following procedure is adopted. Fractional distillation suggests itself as the easiest method, but this must be done cautiously, as the distillation of many compounds is accompanied by decomposition. It is preferable first to shake the mixture with water (water soluble compounds), then with caustic soda (acidic compounds), and finally with dilute hydrochloric acid (basic compounds). In the second case acids and phenols are removed, and may be precipitated by the addition of hydrochloric acid, while in the last case the base extracted may be freed by the addition of alkali. Should this not prove effective, the mixture is distilled on the water-bath to remove any volatile constituent. Should this fail, the mixture is fractionally distilled. When examination shows that one or both constituents are easily

decomposed, the distillation is carried out under reduced pressure.

Other methods are also used. Thus nitrobenzene and quinoline can be separated by acidifying the mixture, and steam distillation, the nitrobenzene passing over in the steam and the quinoline salt remaining in the distillation flask. The quinoline is then isolated by making the solution alkaline. This method of separation is based on the rule that salts are non-volatile, and is important both in qualitative and preparative work.

Liquids are sometimes converted into crystalline derivatives for the purpose of separation. Aromatic amines can be separated from impurities or many other compounds by conversion into picrates which are only moderately soluble in benzene or alcohol, and which crystallise well. The picrates can therefore be readily isolated and purified, and are converted back into the amines by the action of ammonia. Similarly many carbonyl compounds yield bisulphite derivatives with sodium bisulphite. These compounds are insoluble in organic solvents, and yield the carbonyl compound on treatment with dilute acid or aqueous sodium carbonate.

(2) **Solid and Liquid.** The methods outlined above are applicable in this case. Steam distillation or ordinary distillation is often used.

(3) **Two Solids.** Sodium carbonate and then hydrochloric acid are first used to remove any acidic or basic compounds. If this fails small samples of the mixture are shaken with various solvents in the following order—water, ether, alcohol, and benzene. Other solvents may also be tried, *e.g.*, chloroform, carbon tetrachloride, glacial acetic acid, etc. The mixture (0·5 g.) is finely ground and shaken thoroughly with the solvent (2 c.c.) and filtered. The filtrate is evaporated to dryness on the water-bath. If a considerable amount of residue is obtained, its melting point is determined. A sharp melting point indicates that the solvent is suitable for separation. If the melting point is not sharp, the residue is purified by crystallisation, and its melting point again determined. If it is still not sharp, other solvents are tried.

Boiling solvents are often extremely useful. Thus benzoic acid

can be removed from many mixtures by boiling with water and filtering the hot solution. The filtrate on cooling deposits the acid in the crystalline state, while the other compound remains on the filter paper.

Water is sometimes less satisfactory than organic solvents. Thus it removes sugars from mixtures, but has the disadvantage that on evaporation of the water the sugar may be obtained as a syrup which is difficult to purify. It is better in such cases to use ether, which removes many organic compounds but does not dissolve sugars.

Steam distillation is employed to separate many compounds and isomers. *o*-Nitrophenol is easily separated from the *para* compound, as it is volatile in steam, whereas the *para* compound is non-volatile. Salts can be separated from volatile compounds in this way.

Sublimation is sometimes used. Benzoic acid can be separated from cinnamic acid and many substituted benzoic acids by careful sublimation: the sublimate consists of benzoic acid, while the other acid is left as a residue.

Certain mixtures may be separated by the preparation of derivatives of the components. Thus *o*- and *p*-nitrocinnamic acids are separated by conversion into their ethyl esters, which are treated with alcohol. The *ortho* compound dissolves, while the *para* ester is relatively insoluble. The acids are then re-generated by hydrolysis.

An important separation is the isolation of a phenol and a carboxylic acid from a mixture of the two. This is accomplished by means of sodium bicarbonate, which dissolves the acid but not the phenol (unless the latter happens to be a nitrophenol). The mixture is treated with sodium bicarbonate solution until the solution is alkaline and is then extracted with ether, which on evaporation yields the phenol, often as an oil. This quickly solidifies, and may be identified as the acetyl or benzoyl derivative. The alkaline portion on acidification with hydrochloric acid yields the carboxylic acid.

Other general methods of separation include that of chromatographic adsorption, which in recent years has been used with great success, especially with mixtures which could not be separ-

ated by ordinary means. A considerable technique is necessary, but there can be no doubt that the method will be widely used and developed in the next few years.

References

Zechmeister and Cholnoky, *Die Chromatographische Adsorptionsmethode.*

Bernhauer, *Einführung in die organisch-chemische Laboratoriumstechnik*, p. 99.

PART B

Explanation of Tables

In this section of the book several hundreds of compounds are classified, each group being arranged in order of boiling points or melting points. A short summary of the properties of each compound and of the derivatives used for its identification is given.

To save space the following abbreviations are adopted. For the most part those used in the *Journal of the Chemical Society* have been employed.

alcoh. . .	alcoholic.
aq. . . .	aqueous.
asym. . .	asymmetric.
b.p. . . .	boiling point.
b.p./10 mm. .	boiling point under 10 mm. pressure.
conc. . .	concentrated.
d . . .	specific gravity at 20° referred to water at 4°—*i.e.*, d^{20}_{4}, unless otherwise stated.
d (after m.p.) .	with decomposition.
d- . . .	dextro (cf., however, sugars).
dil. . . .	dilute.
dl- . . .	racemic.
f.p. . . .	freezing point.
fum. . .	fuming.
l- . . .	laevo-.
m- . . .	meta-.
m.p. . .	melting point.
n . . .	refractive index.
n- . . .	normal.
neut. equiv. .	neutral equivalent.
o- . . .	ortho-.
p- . . .	para-.
ppt. . .	precipitate.
ψ- . . .	pseudo.
r- . . .	racemic.

s- . . .	symmetrical.
sec.- . .	secondary.
soln. . .	solution.
sym.- . .	symmetrical.
tert.- . .	tertiary.

Unless otherwise stated, "acid" means concentrated acid. Thus acetic acid means glacial acetic acid.

"Sublimes" means that the compound can be sublimed at atmospheric pressure for purification purposes with little or no decomposition.

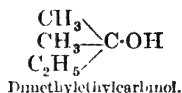
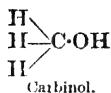
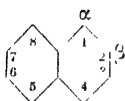
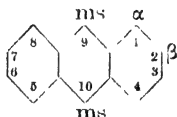
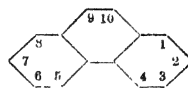
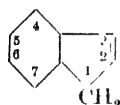
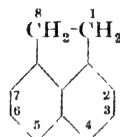
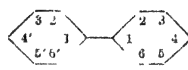
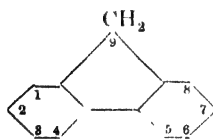
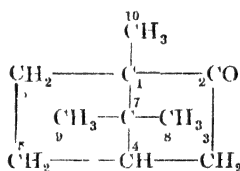
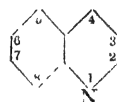
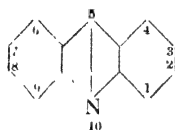
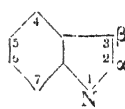
Compounds and derivatives are colourless unless a colour is stated. Most of the derivatives quoted are crystallised from ethyl alcohol, but where other solvents are recommended, these are given in brackets.

Nomenclature

The nomenclature of organic compounds is not always a simple matter, as the student will find when he first consults such reference books as Beilstein or Heilbron. This is partly due to the fact that no system of nomenclature has been universally adopted, and partly to the inherent difficulty in naming complicated compounds. The matter, however, has been simplified to some extent by the adoption of certain conventions (for an authoritative discussion on the subject see Smith, *J.*, 1936, 1067). For instance, the compound $NO_2 \cdot C_6H_4 \cdot Br$ may be called bromonitrobenzene or nitrobromobenzene. The convention generally accepted places halogen before nitro and therefore the compound is listed in Beilstein as bromonitrobenzene and the student will look in vain for nitrobromobenzene. With a little trouble the main conventions may be learned, and the task of naming a compound or finding it in the literature is simplified.

The compounds given in this book are for the most part easily named, but in cases of difficulty the easiest method has been adopted. Thus with the higher alcohols the carbinol system is used—*i.e.*, the alcohols are regarded as substituted methyl alcohols or substituted carbinols. For example, $(CH_3)_2C(OH) \cdot C_2H_5$, known as tertiary amyl alcohol or amylene hydrate, is listed as dimethylethylcarbinol.

$$\begin{matrix} H \\ H \\ H \end{matrix} \Big\rangle C \cdot OH \qquad \qquad \begin{matrix} CH_3 \\ CH_3 \\ C_2H_5 \end{matrix} \Big\rangle C \cdot OH$$

Carbinol. Dimethylethylcarbinol.

It is also essential to know the numbering of ring compounds, and the systems used in the more important cases are given below.

Naphthalene. Anthracene. Phenanthrene.

Indene. Acenaphthene. Diphenyl.

Fluorene. Camphor. Quinoline.

Isoquinoline. Acridine. Indole.

Paraffins and Cycloparaffins

(General tests, see pp. 48–49)

b.p.

Gas Methane, CH_4.

Burns with weakly luminous flame.

Gas Ethane, $CH_3 \cdot CH_3$.

Burns with luminous flame.

b.p.

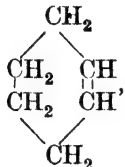
Gas *n*-Propane, $CH_3{\cdot}CH_2{\cdot}CH_3$.
Burns with luminous flame.

Gas *n*-Butane, $CH_3(CH_2)_2CH_3$.
Burns with luminous flame.

36° *n*-Pentane, $CH_3(CH_2)_3CH_3$, d 0·631, n_D^{20} 1·3564.
Burns with luminous smoky flame.

69° *n*-Hexane, $CH_3(CH_2)_4CH_3$, d 0·6603, n_D^{20} 1·376.

81° Cyclohexane, f.p. 6·5°, d 0·779, n_D^{20} 1·4273.
Burns with luminous smoky flame.
Does not react with cold fuming HNO_3 (cf. benzene).

98° *n*-Heptane, $CH_3(CH_2)_5CH_3$, d 0·6837, n_D^{20} 1·385.
Burns with luminous smoky flame.

Unsaturated Hydrocarbons

(General tests, see p. 49)

Gases and Liquids

Gas Ethylene, $CH_2{=}CH_2$.
Burns with luminous flame.
With bromine water forms ethylene dibromide, a heavy oil, which is identified as the *iso*thiourea picrate—yellow crystals, m.p. 260°.

Gas Acetylene, $CH{\equiv}CH$.
Burns with luminous flame.

83° Cyclohexene, d 0·810, n_D^{20} 1·4451.

Decolorises bromine in CCl_4.

146° Styrene, $C_6H_5{\cdot}CH{=}CH_2$, d 0·903, n_D^{17} 1·5485.

b.p.

Bromination (glacial acetic acid) ⟶ styrene dibromide, prisms, m.p. 77°.

Polymerises immediately to a glassy mass on addition of a drop of conc. H_2SO_4.

155° *d*-α-Pinene, $C_{10}H_{16}$, d 0·8667.

Characteristic odour resembling camphor.

160° *dl*-Camphene, $C_{10}H_{16}$, m.p. 50°.

Characteristic odour. Sublimes readily.

176° *d*-Limonene, $C_{10}H_{16}$, d 0·8403.

Pleasant odour of lemons.

182° Indene, d 0·9915, n_D^8 1·571.

Decolorises bromine in CCl_4 immediately.

Picrate explosive.

1 : 3 : 5-Trinitrobenzene in absolute alcohol ⟶ molecular compound, yellow needles, m.p. 101°.

Solid

m.p.

125° Stilbene, $C_6H_5 \cdot CH{=}CH \cdot C_6H_5$.

Sublimes. Volatile in steam.

Bromination (glacial acetic acid) ⟶ stilbene dibromide: purified by washing with boiling alcohol: m.p. 237°.

Aromatic Hydrocarbons

(General tests, see pp. 49–51. Colour tests, see p. 44)

Liquids

b.p.

80° Benzene, m.p. 5·6°, d 0·878.

Differs from cyclohexane (b.p. 81°) by reacting briskly with cold fuming HNO_3.

Nitration (conc. H_2SO_4 and fuming HNO_3) ⟶ 1 : 3-dinitrobenzene, needles or prisms, m.p. 90°.

Picrate unstable.

b.p.

111° Toluene, $C_6H_5 \cdot CH_3$, d 0·866.

Nitration (conc. H_2SO_4 and fuming HNO_3) ⟶ 2 : 4-dinitrotoluene, prisms, m.p. 72°.

Oxidation with $KMnO_4$ (3 hrs.), or with HNO_3 ⟶ benzoic acid, plates (water), m.p. 122°.

136° Ethylbenzene, $C_6H_5 \cdot C_2H_5$, d 0·868.

Oxidation (CrO_3 in acetic acid) ⟶ acetophenone, which is obtained as an oil by the addition of water to the oxidising mixture and is identified as the dinitrophenylhydrazone—orange-red needles (acetic acid), m.p. 249°.

138° *p*-Xylene, $CH_3 \cdot C_6H_4 \cdot CH_3$, f.p. 13°, d 0·861.

Nitration (conc. H_2SO_4 and fuming HNO_3) ⟶ 2 : 3 : 5-trinitro-*p*-xylene, plates, m.p. 139°.

Oxidation ($KMnO_4$) ⟶ terephthalic acid.

Oxidation (HNO_3—2 hrs. at 100°) ⟶ *p*-toluic acid, m.p. 181°.

139° *m*-Xylene, $CH_3 \cdot C_6H_4 \cdot CH_3$, d 0·865.

Nitration (conc. H_2SO_4 and fuming HNO_3) ⟶ 2 : 4 : 6-trinitro-*m*-xylene, hexagonal plates (acetic acid), m.p. 182°.

Oxidation ($KMnO_4$—2 hrs.) ⟶ isophthalic acid, needles (water), sublimes above 300°.

Oxidation (HNO_3—2 hrs. at 100°) ⟶ *m*-toluic acid, m.p. 112°.

144° *o*-Xylene, $CH_3 \cdot C_6H_4 \cdot CH_3$, d 0·879.

Nitration (conc. H_2SO_4 and fuming HNO_3) ⟶ oil.

Oxidation ($KMnO_4$—2 hrs.) ⟶ phthalic acid, m.p. 195°.

Oxidation (HNO_3—2 hrs. at 100°) ⟶ *o*-toluic acid, m.p. 107°.

152° *iso*Propylbenzene, $C_6H_5 \cdot CH<^{CH_3}_{CH_3}$, d 0·864, n_D^{20} 1·4930.

159° Propylbenzene, $C_6H_5 \cdot C_3H_7$, d 0·862.

Oxidation (HNO_3) ⟶ benzoic acid, plates (water), m.p. 122°.

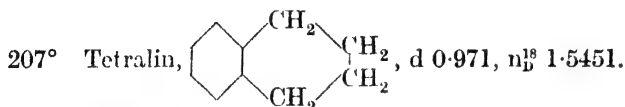
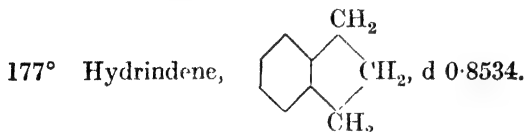
b.p.

162° 1-Methyl-4-ethylbenzene, $CH_3 \cdot C_6H_4 \cdot C_2H_5$, d 0·862.
Oxidation ($KMnO_4$—6 hrs.) ⟶ terephthalic acid (identified as dimethyl ester).
Oxidation (HNO_3—2 hrs.) ⟶ terephthalic acid (identified as dimethyl ester).

165° Mesitylene, d 0·8634.
Nitration (conc. H_2SO_4 and fuming HNO_3) ⟶ trinitromesitylene, yellow needles (glacial acetic acid), m.p. 235°.

177° *p*-Cymene, $(CH_3)_2CH \cdot C_6H_4 \cdot CH_3$, d 0·8570.
Oxidation (HNO_3—2 hrs. at 100°) ⟶ terephthalic acid (identified as dimethyl ester).

177° Hydrindene, $C_6H_4(CH_2)_2CH_2$ [benzene ring fused to CH₂–CH₂–CH₂ ring], d 0·8534.

207° Tetralin, $C_6H_4(CH_2)_4$ [benzene ring fused to CH₂–CH₂–CH₂–CH₂ ring], d 0·971, n_D^{18} 1·5451.

243° 1-Methylnaphthalene, $C_{10}H_7 \cdot CH_3$.
Volatile in steam.
Picrate : yellow needles, m.p. 143°.
sym.-Trinitrobenzene derivative : pale yellow needles, m.p. 154°.

Solids

m.p.

26–27° Diphenylmethane, $C_6H_5 \cdot CH_2 \cdot C_6H_5$.
Nitration (conc. H_2SO_4 and fuming HNO_3) ⟶ 2 : 4 : 2′ : 4′-tetranitrodiphenylmethane, prisms (acetic acid), m.p. 172°.
Oxidation (HNO_3—1 hr. at 150°) ⟶ benzophenone (identified as dinitrophenylhydrazone).

35° 2-Methylnaphthalene, $C_{10}H_7 \cdot CH_3$.
Picrate : yellow needles, m.p. 115°.

m.p.

Trinitrobenzene derivative : pale yellow needles, m.p. 125°.

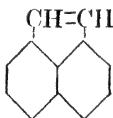
52° Dibenzyl, $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot C_6H_5$.
Oxidised with difficulty to benzoic acid.

71° Diphenyl, $C_6H_5 \cdot C_6H_5$, b.p. 254°.
Sublimes. Volatile in steam.
Nitration (fuming HNO_3 in acetic acid) ⟶ 4 : 4′-dinitrodiphenyl, needles (acetic acid), m.p. 234°.

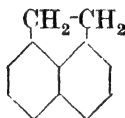
80° Naphthalene,

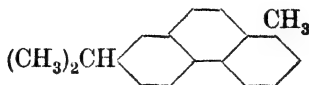
Sublimes. Volatile in steam.
Picrate : yellow needles, m.p. 149°.
Trinitrobenzene compound : pale yellow needles, m.p. 154°.

93° Triphenylmethane, $(C_6H_5)_3CH$.
Oxidises to triphenylcarbinol. Triphenylmethane (0·3 g.) is boiled with 5 c.c. conc. HNO_3 and 1 c.c. water for 10 mins. The mixture is poured into water, and the ppt. recrystallised from alcohol. Prisms, m.p. 164°.

92° Acenaphthylene,

Yellow.
Picrate : chocolate-coloured prisms, m.p. 201°.

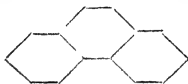
95° Acenaphthene,

CH_2-CH_2

Sublimes.
Picrate : orange needles, m.p. 162°.
Trinitrobenzene compound : yellow needles, m.p. 168°.

99° Retene, $(CH_3)_2CH$ … CH_3

Sublimes.

m.p.

Picrate : orange needles, m.p. 123°.
Trinitrobenzene compound : m.p. 139°.
Quinone : orange plates, m.p. 196°.

100° Phenanthrene,

Sublimes.
Picrate : orange needles, m.p. 144°.
Trinitrobenzene derivative : yellow needles, m.p. 158°.
Quinone : orange prisms (acetic acid), m.p. 208°.

110° Fluoranthene,

Sublimes.
Heated with conc. H_2SO_4, gives a greenish-blue coloration.
Picrate (prepared in acetic acid solution) : orange needles (acetic acid), m.p. 186°.

116° Fluorene,

Sublimes. No fluorescence when pure.
Conc. H_2SO_4 produces a beautiful blue colour on warming.
Bromination (glacial acetic acid) ⟶ 2 : 7-dibromofluorene, needles, m.p. 165°.
Nitration (fuming HNO_3 in acetic acid) ⟶ 2 : 7-dinitrofluorene, chars at high temp. without melting.
Picrate unstable.

155° Pyrene,

Sublimes. Colourless, but generally obtained as a pale yellow compound.
Picrate (prepared in acetic acid) : red needles (acetic acid), m.p. 223°.

m.p.

Trinitrobenzene compound (prepared in acetic acid): orange needles, m.p. 253°.

188° 2 : 2′-Dinaphthyl, $C_{10}H_7 \cdot C_{10}H_7$.

Picrate: orange prisms, m.p. 184°.

217° Anthracene,

Sublimes. Usually obtained as pale yellow substance, but is colourless when pure.

Bromination (acetic acid) ⟶ 9 : 10-dibromoanthracene, yellow needles (acetic acid), m.p. 222°.

Picrate: red needles, m.p. 138°. Unstable and not easily prepared in the pure state.

Trinitrobenzene compound (prepared in benzene solution): m.p. 164°.

Oxidation (CrO_3 in acetic acid) ⟶ anthraquinone, yellow prisms, m.p. 286°.

254° Chrysene,

Sublimes.

Bromination (acetic acid) ⟶ dibromo derivative, yellow needles, m.p. 275°.

Picrate (prepared in benzene): orange needles, m.p. not sharp.

Trinitrobenzene derivative (prepared in benzene solution): yellow needles, m.p. 190°. Decomposes on crystallisation from alcohol.

Oxidation (CrO_3 in acetic acid) ⟶ quinone, orange prisms (acetic acid), m.p. 239°.

Halogen Derivatives of the Hydrocarbons

(General tests, see pp. 51–52)

Liquids

b.p.

12° Ethyl chloride, C_2H_5Cl.

b.p.

39° Ethyl bromide, C_2H_5Br, d 1·4600.
Alkyl-*iso*thiourea picrate : yellow prisms, m.p. 188°.

40° Methylene chloride, CH_2Cl_2, d_4^{15} 1·3348.

43° Methyl iodide, CH_3I, d 2·278.
Alkyl-*iso*thiourea picrate : yellow prisms, m.p. 224°.

46° *n*-Propyl chloride, C_3H_7Cl, d 0·892.

45° Allyl chloride, $CH_2:CH{\cdot}CH_2Cl$, d 0·9379.
Alkyl-*iso*thiourea picrate : yellow prisms, m.p. 154°.

59° *iso*Propyl bromide, $(CH_3)_2CHBr$, d 1·310.
Alkyl-*iso*thiourea picrate (3 hrs.) : orange needles, m.p. 196°.

61° Chloroform, $CHCl_3$, d 1·489.
Positive carbylamine test.
Reduces boiling Fehling's solution.

71° Allyl bromide, $CH_2:CH{\cdot}CH_2Br$, d 1·389.
Alkyl-*iso*thiourea picrate : yellow prisms, m.p. 154°.

71° *n*-Propyl bromide, C_3H_7Br, d 1·3538.
Alkyl-*iso*thiourea picrate : yellow prisms, m.p. 177°.

72° Ethyl iodide, C_2H_5I, d 1·934.
Alkyl-*iso*thiourea picrate : yellow prisms, m.p. 188°.

77° Carbon tetrachloride, CCl_4, d_4^{25} 1·5844.
Unlike chloroform, does not reduce boiling Fehling's solution.

78° *n*-Butyl chloride, C_4H_9Cl, d 0·8845.
Alkyl-*iso*thiourea picrate (2 hrs.) : yellow needles, m.p. 177°.

84° Ethylene dichloride, $CH_2Cl{\cdot}CH_2Cl$, d 1·2521.

85° Fluorobenzene, C_6H_5F, d 1·0236.

88° Trichlorethylene, $CHCl:CCl_2$, d 1·477.

90° *iso*Propyl iodide, $(CH_3)_2CHI$, d 1·7033.
Alkyl-*iso*thiourea picrate : orange plates, m.p. 196°.

102° *n*-Propyl iodide, C_3H_7I, d 1·7428.
Alkyl-*iso*thiourea picrate : yellow plates, m.p. 177°.

102° *n*-Butyl bromide, C_4H_9Br, d 1·2745.
Alkyl-*iso*thiourea picrate : yellow needles, m.p. 177°.

103° Allyl iodide, $CH_2:CH{\cdot}CH_2I$, d 1·848.
Alkyl-*iso*thiourea picrate : yellow prisms, m.p. 154°.

b.p.

120° *sec*.-Butyl iodide, $CH_3{\cdot}CH_2{\cdot}CHI{\cdot}CH_3$, d 1·595.
Alkyl-*iso*thiourea picrate (1 hr.): yellow needles, m.p. 166°.

120° *iso*Butyl iodide, $(CH_3)_2CH{\cdot}CH_2I$, d 1·605.
Alkyl-*iso*thiourea picrate: yellow prisms, m.p. 167°.

121° *iso*Amyl bromide, $(CH_3)_2CH{\cdot}CH_2{\cdot}CH_2Br$, d_4^{15} 1·2095.
Alkyl-*iso*thiourea picrate: yellow prisms, m.p. 173°.

130° *n*-Butyl iodide, C_4H_9I, d 1·616.
Alkyl-*iso*thiourea picrate: yellow needles, m.p. 177°.

130° *n*-Amyl bromide, $CH_3{\cdot}(CH_2)_3{\cdot}CH_2Br$, d 1·223.
Alkyl-*iso*thiourea picrate: yellow prisms, m.p. 154°.

132° Ethylene dibromide, $CH_2Br{\cdot}CH_2Br$, d 2·1785.
Alkyl-*iso*thiourea picrate: yellow plates, m.p. 260°.

132° Chlorobenzene, $C_6H_5{\cdot}Cl$, d 1·107.
Nitration (H_2SO_4 and fuming HNO_3) ⟶ 1-chloro-2 : 4-dinitrobenzene, prisms, m.p. 53°.

148° *iso*Amyl iodide, $(CH_3)_2CH{\cdot}CH_2{\cdot}CH_2I$, d 1·510.
Alkyl-*iso*thiourea picrate: yellow prisms, m.p. 173°.

150° Bromoform, $CHBr_3$, f.p. 8°, d 2·890.
Positive carbylamine test.

156° *n*-Amyl iodide, $CH_3{\cdot}(CH_2)_3{\cdot}CH_2I$, d 1·517.
Alkyl-*iso*thiourea picrate: yellow prisms, m.p. 154°.

156° Bromobenzene, $C_6H_5{\cdot}Br$, d 1·4950.
Nitration (H_2SO_4 and fuming HNO_3) ⟶ 1-bromo-2 : 4-dinitrobenzene, prisms, m.p. 75°.

156° *n*-Hexyl bromide, $CH_3{\cdot}(CH_2)_4{\cdot}CH_2Br$, d 1·1763.
Alkyl-*iso*thiourea picrate: yellow plates, m.p. 157°.

159° *o*-Chlorotoluene, $CH_3{\cdot}C_6H_4{\cdot}Cl$, d 1·080.
Oxidation ($KMnO_4$—2 hrs.) ⟶ *o*-chlorobenzoic acid, needles (water), m.p. 142°.

162° *m*-Chlorotoluene, $CH_3{\cdot}C_6H_4{\cdot}Cl$, d 1·072.
Nitration (conc. H_2SO_4 and fuming HNO_3) ⟶ 3-chloro-4 : 6-dinitrotoluene, prisms, m.p. 91°.
Oxidation ($KMnO_4$—2 hrs.) ⟶ *m*-chlorobenzoic acid, needles (water), m.p. 158°. As the m.p. of *m*-bromobenzoic acid is 155°, a mixed m.p. with a specimen of *m*-chlorobenzoic acid is necessary.

b.p.

162° *p*-Chlorotoluene, $CH_3 \cdot C_6H_4 \cdot Cl$, m.p. 8°, d_4^{18} 1·071.
  Oxidation ($KMnO_4$—2 hrs.) ⟶ *p*-chlorobenzoic acid, needles (water), m.p. 243°.

173° *m*-Dichlorobenzene, $Cl \cdot C_6H_4 \cdot Cl$, d 1·2881, n_D^{17} 1·548.

179° *o*-Dichlorobenzene, $Cl \cdot C_6H_4 \cdot Cl$, d 1·3048.

179° Benzyl chloride, $C_6H_5 \cdot CH_2Cl$, d_{20}^{20} 1·1002.
  Alkyl-*iso*thiourea picrate; yellow prisms, m.p. 188°.
  Quaternary ammonium compound: benzyl chloride and dimethylaniline are mixed, and the solution is allowed to stand overnight. The ppt. is washed with ether, yielding plates, m.p. 110°.
  Oxidation ($KMnO_4$—½ hr.) ⟶ benzoic acid, plates (water), m.p. 122°.

182° *o*-Bromotoluene, $CH_3 \cdot C_6H_4 \cdot Br$, d 1·422.
  Oxidation (HNO_3—3 hrs. at 200°) ⟶ *o*-bromobenzoic acid, m.p. 150°.

184° *p*-Bromotoluene, $CH_3 \cdot C_6H_4 \cdot Br$, m.p. 28°.
  Oxidation ($KMnO_4$—1·5 hr.) ⟶ *p*-bromobenzoic acid, m.p. 254°. Prisms from aq. alcohol.

184° *m*-Bromotoluene, $CH_3 \cdot C_6H_4 \cdot Br$, d 1·140.
  Oxidation ($KMnO_4$—3 hrs.) ⟶ *m*-bromobenzoic acid, plates (water), m.p. 155°. A mixed m.p. with a specimen of *m*-bromobenzoic acid is necessary as the corresponding chloro acid has nearly the same m.p.

189° Iodobenzene, $C_6H_5 \cdot I$, d 1·832.
  Nitration (conc. H_2SO_4 and conc. HNO_3) ⟶ *p*-iodonitrobenzene, needles, m.p. 174°.
  Nitration (conc. H_2SO_4 and fuming HNO_3) ⟶ 1-iodo-2 : 4-dinitrobenzene, prisms, m.p. 89°.

199° Benzyl bromide, $C_6H_5 \cdot CH_2Br$, d 1·4380.
  Alkyl-*iso*thiourea picrate: yellow prisms, m.p. 188°.
  Oxidation ($KMnO_4$—½ hr.) ⟶ benzoic acid, plates (water), m.p. 122°.

211° *o*-Iodotoluene, $CH_3 \cdot C_6H_4 \cdot I$, d 1·698.
  Resistant to oxidation with $KMnO_4$.
  Oxidation (HNO_3—3 hrs. at 200°) ⟶ *o*-iodobenzoic acid, m.p. 162°.

b.p.

211° *p*-Iodotoluene, $CH_3·C_6H_4·I$, m.p. 36°.
Resistant to oxidation with $KMnO_4$.
Oxidation (HNO_3—3 hrs. at 200°) ⟶ *p*-iodobenzoic acid, m.p. 270°, methyl ester, m.p. 114°.

213° *m*-Iodotoluene, $CH_3·C_6H_4·I$, d 1·698.
Resistant to oxidation with $KMnO_4$.
Oxidation (HNO_3—3 hrs. at 200°) ⟶ *m*-iodobenzoic acid, m.p. 182°.

214° Benzal chloride, $C_6H_5·CHCl_2$.
Oxidation ($KMnO_4$—1 hr.) ⟶ benzoic acid, plates (water), m.p. 122°.
Hydrolysis ⟶ benzaldehyde. A small quantity of benzal chloride is heated for 10 secs. with 3 c.c. conc. H_2SO_4 and allowed to stand at room temp. for 15 mins. A little dinitrophenylhydrazine is added, the soln. is gently heated and poured into alcohol. Benzaldehyde dinitrophenylhydrazone separates. Orange prisms (acetic acid), m.p. 237°.

221° Benzotrichloride, $C_6H_5·CCl_3$.
Nitration (conc. H_2SO_4 and fuming HNO_3) ⟶ *m*-nitrobenzoic acid, m.p. 142°.
Oxidation ($KMnO_4$—1 hr.) ⟶ benzoic acid, plates (water), m.p. 122°.
Hydrolysis ⟶ benzoic acid. The compound is heated gently for 5 mins. with conc. H_2SO_4, and is then carefully poured into water. Benzoic acid separates; plates (water), m.p. 122°.

258° α-Chloronaphthalene, $C_{10}H_7·Cl$.
Picrate: yellow needles, m.p. 137°.

281° α-Bromonaphthalene, $C_{10}H_7·Br$, m.p. 5°, d_4^{20} 1·476.
Picrate: yellow needles, m.p. 134°.

305° α-Iodonaphthalene, $C_{10}H_7·I$, d^{15} 1·7344.
Picrate: yellow needles, m.p. 128°.

Solids

m.p.

53° *p*-Dichlorobenzene, $Cl·C_6H_4·Cl$.
Nitration (fuming HNO_3—2 mins.) ⟶ 1 : 4-dichloro-2-nitrobenzene, needles, m.p. 56°.

m.p.

55° β-Iodonaphthalene, $C_{10}H_7 \cdot I$.
Volatile in steam.
Picrate : yellow needles, m.p. 95°.

59° β-Bromonaphthalene, $C_{10}H_7 \cdot Br$.
Picrate : yellow needles, m.p. 79°.

61° β-Chloronaphthalene, $C_{10}H_7 \cdot Cl$.
Picrate : yellow needles, m.p. 81°.

89° *p*-Dibromobenzene, $Br \cdot C_6H_4 \cdot Br$, b.p. 219°.
Nitration (fuming HNO_3—2 mins.) ⟶ 1 : 4-dibromo-2-nitrobenzene, needles, m.p. 84°.

113° Triphenylchloromethane, $(C_6H_5)_3C \cdot Cl$.
Hydrolysis ⟶ triphenylcarbinol. The chloro-compound is boiled with water (10 mins.). The triphenylcarbinol so obtained is recrystallised thrice from aq. alcohol : prisms, m.p. 164°.

119° Iodoform, CHI_3.
Sublimes. Characteristic odour.
Quinoline compound : formed by allowing an ethereal soln. of iodoform and quinoline to stand at room temp. : plates, m.p. 65° (d).

187° Hexachloroethane, $CCl_3 \cdot CCl_3$.
Sublimes.

Nitro-Compounds

(General tests, see pp. 52–53. Colour tests, see p. 45)

Liquids

b.p.

101° Nitromethane, CH_3NO_2, d_4^{25} 1·1311.

113° Chloropicrin, CCl_3NO_2, d 1·692.
Acrid odour.

113° Nitroethane, $CH_3CH_2NO_2$, d_4^{15} 1·056.

211° Nitrobenzene, $C_6H_5 \cdot NO_2$, m.p. 6°, d_4^{25} 1·1985.
Yellow liquid. Odour of oil of bitter almonds.
Nitration (conc. H_2SO_4 and fuming HNO_3) ⟶ *m*-dinitrobenzene, colourless needles or prisms, m.p. 90°.

222° *o*-Nitrotoluene, $CH_3 \cdot C_6H_4 \cdot NO_2$.
Yellow liquid. Odour of oil of bitter almonds.

b.p.

Nitration (conc. H_2SO_4 and fuming HNO_3) ⟶ 2 : 4-dinitrotoluene, needles, m.p. 72°.

Reduction (Sn and HCl) ⟶ *o*-toluidine : benzoyl derivative, prisms (acetic acid), m.p. 143°.

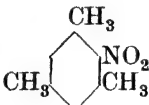
226° (d) Phenylnitromethane, $C_6H_5CH_2NO_2$.

Yellow liquid, slowly soluble in aq. alkali.

231° *m*-Nitrotoluene, $CH_3 \cdot C_6H_4 \cdot NO_2$, m.p. 16°.

Yellow liquid. Odour of oil of bitter almonds.

Oxidation (HNO_3—3 hrs. at 150°) ⟶ *m*-nitrobenzoic acid, m.p. 142°.

Reduction (Sn and HCl) ⟶ *m*-toluidine : benzoyl derivative, plates, m.p. 125°.

Solids

m.p.

37° 2-Nitrodiphenyl, $C_6H_5 \cdot C_6H_4 \cdot NO_2$.

Pale yellow. Volatile in steam.

Reduction (Sn and HCl) ⟶ 2-aminodiphenyl : benzoyl derivative, needles, m.p. 102°.

44° Nitromesitylene,

Nitration (fuming HNO_3 and conc. H_2SO_4) ⟶ trinitromesitylene, elongated prisms (acetic acid), m.p. 239°.

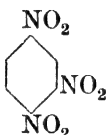
Reduction (Sn and HCl) ⟶ mesidine : benzoyl derivative, prisms, m.p. 206°.

52° *p*-Nitrotoluene, $CH_3 \cdot C_6H_4 \cdot NO_2$, b.p. 238°.

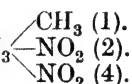
Pale yellow. Odour of oil of bitter almonds.

Oxidation ($KMnO_4$—2 hrs.) ⟶ *p*-nitrobenzoic acid, plates (aq. alcohol), m.p. 242°.

Nitration (fuming HNO_3 and conc. H_2SO_4) ⟶ 2 : 4-dinitrotoluene, needles, m.p. 72°.

58° α-Nitro-β-phenylethylene, $C_6H_5 \cdot CH{:}CH \cdot NO_2$.

Bromination (acetic acid) ⟶ dibromide after 3 hrs. : hexagonal prisms, m.p. 86°.

m.p.

58° 3-Nitrodiphenyl, $C_6H_5 \cdot C_6H_4 \cdot NO_2$.

Orange yellow. Volatile in superheated steam.

Reduction (Sn and HCl) ⟶ 3-aminodiphenyl: acetyl derivative, plates (aq. alcohol), m.p. 148°.

58° 1 : 2 : 4-Trinitrobenzene, $C_6H_3(NO_2)_3$ [ring structure with NO_2 at top, right and bottom]

Pale yellow.

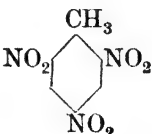
Methylamine (alcoholic soln.) ⟶ immediate ppt. of 2 : 4-dinitromethylaniline, yellow needles, m.p. 175°.

59° α-Nitronaphthalene, $C_{10}H_7 \cdot NO_2$.

Pale yellow. With H_2SO_4 gives red colour.

s-Trinitrobenzene ⟶ molecular compound: prisms, m.p. 72°.

Reduction (Sn and HCl) ⟶ α-naphthylamine, prisms (aq. alcohol), m.p. 50°.

72° 2 : 4-Dinitrotoluene, $C_6H_3 \begin{cases} CH_3 \ (1). \\ NO_2 \ (2). \\ NO_2 \ (4). \end{cases}$

Molecular compound with naphthalene: needles, m.p. 60°.

79° β-Nitronaphthalene, $C_{10}H_7 \cdot NO_2$.

Pale yellow.

Reduction (Sn and HCl) ⟶ β-naphthylamine: acetyl derivative, m.p. 136°.

81° 2 : 4 : 6-Trinitrotoluene (T.N.T.), [ring structure with CH_3 at top, NO_2 at left, right and bottom]

Pale yellow. Explosive on detonation.

Molecular compound with naphthalene: prisms, m.p. 97°.

90° *m*-Dinitrobenzene, $NO_2 \cdot C_6H_4 \cdot NO_2$.

Colourless. Volatile in steam.

m.p.

Molecular compound with naphthalene: needles, m.p. 52°.

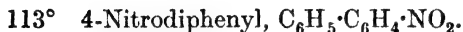
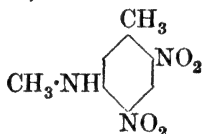
104° 2 : 4 : 5-Trinitrotoluene,

CH_3 NO_2 NO_2 NO_2

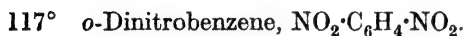
Pale yellow.

With methylamine in alcoholic solution the 5-nitro group is replaced by $NH{\cdot}CH_3$ giving yellow needles, m.p. 174°, *i.e.*,

CH_3 NO_2 $CH_3{\cdot}NH$ NO_2

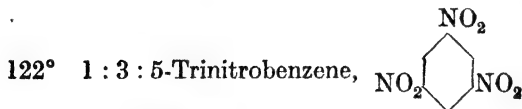
113° 4-Nitrodiphenyl, $C_6H_5{\cdot}C_6H_4{\cdot}NO_2$.

Pale yellow.

Reduction (Sn and HCl) ⟶ 4-aminodiphenyl : acetyl derivative, needles, m.p. 171°.

117° *o*-Dinitrobenzene, $NO_2{\cdot}C_6H_4{\cdot}NO_2$.

Colourless. Volatile in steam.

Reduction (Sn and HCl) ⟶ *o*-phenylenediamine : diphenylquinoxaline, needles (acetic acid), m.p. 124°.

122° 1 : 3 : 5-Trinitrobenzene,

NO_2 NO_2 NO_2

Colourless.

Molecular compound with anthracene in benzene solution : orange prisms, m.p. 164° ; unstable to water.

171° 1 : 8-Dinitronaphthalene,

NO_2 NO_2

Pale yellow.

m.p.

174° *p*-Dinitrobenzene, $NO_2 \cdot C_6H_4 \cdot NO_2$.
Colourless. Volatile in steam. Sublimes.
Molecular compound with naphthalene (acetic acid as solvent), needles, m.p. 118°.

239° Trinitromesitylene, $C_6(CH_3)_3(NO_2)_3$ (ring: CH_3 at top; NO_2 and CH_3 on left; NO_2 and CH_3 on right; NO_2 at bottom).
Colourless.

Halogen-substituted Nitro-Compounds

33° *o*-Chloronitrobenzene, $Cl \cdot C_6H_4 \cdot NO_2$.
Pale yellow.
Nitration (conc. H_2SO_4 and fuming HNO_3) ⟶ 1-chloro-2 : 4-dinitrobenzene, prisms, m.p. 53°.
Reduction ⟶ *o*-chloraniline : benzoyl derivative, prisms, m.p. 99°.

39° *m*-Iodonitrobenzene, $I \cdot C_6H_4 \cdot NO_2$.
Yellow.
Reduction ⟶ *m*-iodoaniline : acetyl derivative, m.p. 120°.

43° *o*-Bromonitrobenzene, $Br \cdot C_6H_4 \cdot NO_2$.
Nitration (conc. H_2SO_4 and fuming HNO_3) ⟶ 1-bromo-2 : 4-dinitrobenzene, hexagonal prisms, m.p. 75°.

45° *m*-Chloronitrobenzene, $Cl \cdot C_6H_4 \cdot NO_2$.
Reduction (Sn and HCl) ⟶ *m*-chloroaniline : benzoyl derivative, plates (aq. alcohol), m.p. 121°.

49° *o*-Nitrobenzyl chloride, $NO_2 \cdot C_6H_4 \cdot CH_2Cl$.
1 g. of the compound heated with 10 c.c. NaOH solution and 5 c.c. alcohol for 1 min. gives a ppt. of 2 : 2′-dinitrostilbene, yellow needles (acetic acid), m.p. 197°.

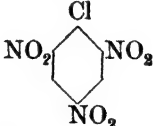
53° 1-Chloro-2 : 4-dinitrobenzene, $C_6H_3 \begin{cases} Cl & (1). \\ NO_2 & (2). \\ NO_2 & (4). \end{cases}$
Pale yellow.

m.p.

Piperidine ⟶ dinitrophenylpiperidine. Chlorodinitrobenzene (0·5 g.) is heated with piperidine (1 c.c.) and alcohol (3 c.c) for 1 min., and the solution is then poured into water containing HCl. The resulting oil is crystallised from alcohol. Orange prisms, m.p. 92°.

54° *o*-Iodonitrobenzene, $I{\cdot}C_6H_4{\cdot}NO_2$.
Yellow.
Nitration (conc. H_2SO_4 and fuming HNO_3) ⟶ 1-iodo-2 : 4-dinitrobenzene, yellow prisms, m.p. 89°.

56° 2 : 5-Dichloronitrobenzene, $C_6H_3\begin{cases} NO_2 & (1). \\ Cl & (2). \\ Cl & (5). \end{cases}$
Pale yellow. Volatile in steam.
Reduction (Sn and HCl) ⟶ 2 : 5-dichloraniline; benzoyl derivative, needles, m.p. 120°.

56° *m*-Bromonitrobenzene, $Br{\cdot}C_6H_4{\cdot}NO_2$.
Reduction (Sn and HCl) ⟶ *m*-bromaniline : benzoyl derivative, prisms, m.p. 137°.

71° *p*-Nitrobenzyl chloride, $NO_2{\cdot}C_6H_4{\cdot}CH_2Cl$.
Oxidation ($KMnO_4$—1 hr.) ⟶ *p*-nitrobenzoic acid, plates (aq. alcohol), m.p. 242°.

75° 1-Bromo-2 : 4-dinitrobenzene, $C_6H_3\begin{cases} Br & (1). \\ NO_2 & (2). \\ NO_2 & (4). \end{cases}$
Pale yellow.
Piperidine ⟶ dinitrophenylpiperidine, orange prisms, m.p. 92° (cf. 1-chloro-2 : 4-dinitrobenzene).

83° Picryl chloride,
Almost colourless.
Piperidine ⟶ trinitrophenylpiperidine, yellow prisms, m.p. 106°.

84° *p*-Chloronitrobenzene, $Cl{\cdot}C_6H_4{\cdot}NO_2$.
Pale yellow.

m.p.

Nitration (conc. H_2SO_4 and fuming HNO_3) ⟶ 1-chloro-2 : 4-dinitrobenzene, prisms, m.p. 53°.

85° 2 : 5-Dibromonitrobenzene, $C_6H_3\begin{cases} NO_2 & (1). \\ Br & (2). \\ Br & (5). \end{cases}$

Yellow.

Reduction (Sn and HCl) ⟶ 2 : 5-dibromaniline : benzoyl derivative, needles, m.p. 153°.

89° 1-Iodo-2 : 4-dinitrobenzene, $C_6H_3\begin{cases} I & (1). \\ NO_2 & (2). \\ NO_2 & (4). \end{cases}$

Yellow.

With methylamine in alcoholic solution rapidly gives a ppt. of 2 : 4-dinitromethylaniline, yellow prisms, m.p. 175°.

99° *p*-Nitrobenzyl bromide, $NO_2{\cdot}C_6H_4{\cdot}CH_2Br$.

Yellow.

With phenol in alkaline solution forms an ether, m.p. 91°.

127° *p*-Bromonitrobenzene, $Br{\cdot}C_6H_4{\cdot}NO_2$.

Nitration (conc. H_2SO_4 and fuming HNO_3) ⟶ 1-bromo-2 : 4-dinitrobenzene, prisms, m.p. 75°.

174° *p*-Iodonitrobenzene, $I{\cdot}C_6H_4{\cdot}NO_2$.

Yellow.

Nitration (conc. H_2SO_4 and fuming HNO_3) ⟶ 1-iodo-2 : 4-dinitrobenzene, yellow prisms, m.p. 89°.

Alcohols

(General tests, see pp. 54–55)

Liquids

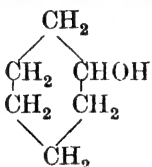
b.p.

65° Methyl alcohol, CH_3OH, d 0·792.

Burns with pale blue flame. Negative iodoform test.

p-Nitrobenzoate, plates, m.p. 96°.

3 : 5-Dinitrobenzoate, plates, m.p. 107°.

b.p.

78° Ethyl alcohol, $CH_3{\cdot}CH_2OH$, d_4^{25} 0·7851.
Burns with pale blue flame. Positive iodoform test.
3 : 5-Dinitrobenzoate, needles, m.p. 93°.

82° *iso*Propyl alcohol, $CH_3{\cdot}CHOH{\cdot}CH_3$, d 0·786.
Burns with luminous flame. Positive iodoform test.
3 : 5-Dinitrobenzoate, needles, m.p. 122°.

82° *tert.*-Butyl alcohol, $(CH_3)_3COH$, m.p. 25°.
Burns with smoky flame.
3 : 5-Dinitrobenzoate, needles, m.p. 142°.

97° *n*-Propyl alcohol, $CH_3{\cdot}CH_2{\cdot}CH_2OH$, d 0·804.
Burns with luminous flame.
3 : 5-Dinitrobenzoate, plates, m.p. 73°.

97° Allyl alcohol, $CH_2{:}CH{\cdot}CH_2OH$, d^{15} 0·8573.
Burns with smoky flame.
3 : 5-Dinitrobenzoate, m.p. 50°, is difficult to obtain in the crystalline state.
Best identified by titration with standard bromine solution.

100° *sec.*-Butyl alcohol, $CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_3$, d 0·808.
Burns with luminous flame.
3 : 5-Dinitrobenzoate, plates, m.p. 76°.

102° Dimethylethylcarbinol, $(CH_3)_2C(OH){\cdot}C_2H_5$, d 0·809.
Burns with smoky flame.
3 : 5-Dinitrobenzoate, plates (ligroin), m.p. 117°.

108° *iso*Butyl alcohol, $(CH_3)_2CH{\cdot}CH_2OH$, d 0·802.
Burns with smoky flame.
3 : 5-Dinitrobenzoate, m.p. 87°.

116° Diethylcarbinol, $C_2H_5{\cdot}CH(OH){\cdot}C_2H_5$, d^{25} 0·815.
3 : 5-Dinitrobenzoate, needles, m.p. 97°.

118° *n*-Butyl alcohol, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2OH$, d 0·810.
3 : 5-Dinitrobenzoate, m.p. 64°.

114° Methyl*iso*propylcarbinol, $(CH_3)_2CH{\cdot}CH(OH){\cdot}CH_3$, d 0·819.
Positive iodoform reaction.
3 : 5-Dinitrobenzoate, m.p. 61°.

120° Methylpropylcarbinol, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_3$, d 0·809.
3 : 5-Dinitrobenzoate, microscopic crystals (petrol ether, b.p. 40–60°), m.p. 62°.

b.p.

128° *sec.*-Butylcarbinol, $CH_3 \cdot CH_2 \cdot CH(CH_3) \cdot CH_2OH$, d 0·816.
3 : 5-Dinitrobenzoate, m.p. 70°.

131° *iso*Butylcarbinol, $(CH_3)_2CH \cdot CH_2 \cdot CH_2OH$, d 0·812.
3 : 5-Dinitrobenzoate, m.p. 62°.

138° *n*-Amyl alcohol, $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2OH$, d 0·817.
Burns with luminous flame.
3 : 5-Dinitrobenzoate, needles (ligroin), m.p. 46°.

161° Cyclohexanol, $CH_2 \langle (CH_2 \cdot CH_2) (CHOH \cdot CH_2) \rangle CH_2$ (ring: CH_2, CH_2, CH_2, CH_2, CH_2, CHOH), m.p. 25°, d 0·945.
Burns with smoky flame.
3 : 5-Dinitrobenzoate, needles, m.p. 112°.

170° Furfuryl alcohol.
Burns with smoky flame. Green colour with HCl. Explodes when treated with conc. HCl.
3 : 5-Dinitrobenzoate, microscopic crystals (aq. methyl alcohol), m.p. 105°.

198° Ethylene glycol, $CH_2OH \cdot CH_2OH$, d 1·115.
Sweet-tasting liquid.
Dibenzoyl derivative, prisms, m.p. 73°.

206° Benzyl alcohol, $C_6H_5 \cdot CH_2OH$, d 1·046.
Oxidation ($KMnO_4$—½ hr.) ⟶ benzoic acid, plates (water), m.p. 122°.
3 : 5-Dinitrobenzoate, needles, m.p. 112°.

220° Phenylethyl alcohol, $C_6H_5 \cdot CH_2 \cdot CH_2OH$, d^{15} 1·024.
Oxidation ($KMnO_4$—½ hr.) ⟶ benzoic acid, plates (water), m.p. 122°.
3 : 5-Dinitrobenzoate, needles, m.p. 107°.

221° Terpineol, d 0·936.

250° Diethylene glycol, $HO \cdot CH_2 \cdot CH_2 \cdot O \cdot CH_2 \cdot CH_2 \cdot OH$.

257° Cinnamyl alcohol, $C_6H_5 \cdot CH{:}CH \cdot CH_2OH$, m.p. 33°.
Decolorises bromine in acetic acid.
Oxidation ($KMnO_4$—½ hr.) ⟶ benzoic acid, plates (water), m.p. 122°.

b.p.

290° Glycerol, $CH_2OH \cdot CH(OH) \cdot CH_2OH$, m.p. 18°.
Sweet-tasting viscous liquid. Hygroscopic.
Tribenzoate (6 mols. benzoyl chloride to 1 mol. glycerol). Crystallised from aq. alcohol and then from petrol ether, b.p. 60–80°, m.p. 76°, prisms. Best prepared by pyridine method.

Solids

m.p.

38° Pinacol, $(CH_3)_2C(OH) \cdot C(OH)(CH_3)_2$.
Camphor odour.
The hydrate is obtained by heating with water: plates, m.p. 55°.

69° Benzhydrol, $(C_6H_5)_2CHOH$.
Deep red colour with conc. H_2SO_4.
When fused with succinic acid for 5 mins. the di-ester of succinic acid is formed: prisms, m.p. 141°.

139° Hydrobenzoin, $C_6H_5 \cdot CHOH \cdot CHOH \cdot C_6H_5$.
Diacetyl derivative: needles, m.p. 134–135° (mixed m.p. necessary; cf. m.p. of hydrobenzoin).

164° Triphenylcarbinol, $(C_6H_5)_3COH$.
Bright yellow colour with conc. H_2SO_4.
Acetyl chloride $\longrightarrow$ triphenylmethyl chloride. The carbinol is warmed with a little acetyl chloride. A soln. is obtained which in a few seconds deposits triphenylmethyl chloride: after pressing on porous plate, m.p. 112°.

166° *d*-Mannitol, $CH_2OH \cdot (CHOH)_4 \cdot CH_2OH$.
Hexa-acetyl derivative: obtained by adding water to the soln. after acetylation, and allowing the mixture to stand for ½ hr. Prisms (water), m.p. 123°.

253° Pentaerythritol, $C(CH_2OH)_4$.
Tetrabenzoate (pyridine method), prisms, m.p. 99°.
Tetra-acetate: needles (water), m.p. 84° after several crystallisations.

Phenols

(General tests, see pp. 55–57. Colour tests, see pp. 33, 40)

Liquids

b.p.

203° *m*-Cresol, $C_6H_4<^{OH}_{CH_3}$, m.p. 12°.

FeCl$_3$: blue (water), green (alcohol).
Benzoyl derivative: prisms, m.p. 55°.
Aryloxyacetic acid: elongated prisms (aq. alcohol), m.p. 102–103°; neut. equiv., 166.

254° Eugenol, $C_{10}H_{12}O_2$.

Odour of oil of cloves.
FeCl$_3$: green (alcohol).
Benzoyl derivative: prisms, m.p. 69°.

270° Isoeugenol, $C_{10}H_{12}O_2$, m.p. 32°.

Odour of oil of cloves. Conc. H_2SO_4 gives red colour.
FeCl$_3$: transient green (alcohol).
Benzoyl derivative: prisms, m.p. 104°.

Solids

m.p.

31° *o*-Cresol, $CH_3 \cdot C_6H_4 \cdot OH$, b.p. 191–192°.

Odour of carbolic. Volatile in steam.
FeCl$_3$: blue (water), green (alcohol).
Aryloxyacetic acid: plates (aq. alcohol), m.p. 151–152°; neut. equiv. 166.

32° Guaiacol, $CH_3O \cdot C_6H_4 \cdot OH$(1 : 2), b.p. 205°.

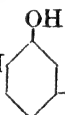
Pleasant odour.
FeCl$_3$: greenish-blue (water).
Benzoate: prisms (aq. alcohol), m.p. 59°.
Bromination (acetic acid) ⟶ tribromoguaiacol, prisms (aq. alcohol), m.p. 116°.
Arylhydroxyacetic acid: prisms (aq. alcohol), m.p. 116°; neut. equiv., 182.

36° *p*-Cresol, $CH_3 \cdot C_6H_4 \cdot OH$, b.p. 202°.

Volatile in steam.
FeCl$_3$: blue (water), green (alcohol).
Benzoyl derivative: prisms, m.p. 71°.

m.p.

Aryloxyacetic acid: prisms (aq. alcohol), m.p. 136°; neut. equiv. 166.

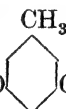
41° Phenol, $C_6H_5{\cdot}OH$, b.p. 182°.

Characteristic odour of carbolic. Volatile in steam.

$FeCl_3$: green (alcohol), violet (water).

Benzoyl derivative: prisms, m.p. 69°.

2 : 4 : 6-Tribromophenol: excess bromine water is added to phenol and the mixture shaken. The white ppt. is washed with sulphurous acid and recrystallised from alcohol: needles, m.p. 95°.

Aryloxyacetic acid: prisms (aq. alcohol), m.p. 98–99°; neut. equiv. 152.

OH

51° Thymol, $(CH_3)_2CH$ —CH₃ , b.p. 234°.

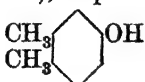
Characteristic odour. Volatile in steam. Conc. H_2SO_4 gives red colour.

$FeCl_3$: transient green (alcohol).

p-Nitrobenzyl ether: prisms, m.p. 85°.

Aryloxyacetic acid: needles (aq. alcohol), m.p. 150°; neut. equiv. 208.

CH_3

58° Orcinol (hydrated), HO OH, m.p. of anhydrous compound, 107°.

Crystallises from water with one mol. water of crystallisation.

Sublimes in vacuo.

$FeCl_3$: dark violet (water).

Dibenzoate: needles, m.p. 88°.

Bromination (acetic acid) ⟶ tribromorcinol, rhombic plates (acetic acid), m.p. 104°.

62° 1 : 2 : 4-Xylenol, CH_3 CH_3 OH

$FeCl_3$: green (alcohol or water).

m.p.

Benzoyl derivative: cubic prisms (aq. alcohol), m.p. 60°. (Mixed m.p. necessary, cf. m.p. of xylenol.)

Aryloxyacetic acid: plates, m.p. 162°; neut. equiv. 180.

87° Saligenin, $HO \cdot C_6H_4 \cdot CH_2OH$(1 : 2).

Sublimes easily. H_2SO_4 gives red coloration.

$FeCl_3$: blue (alcohol), violet (water).

Aniline ⟶ *o*-hydroxybenzylaniline: 0·2 g. saligenin is heated for 10 mins. with aniline, and the solution then diluted with dil. acetic acid. The ppt. is recrystallised from aq. alcohol, m.p. 108°.

94° α-Naphthol, $C_{10}H_7 \cdot OH$.

Sublimes. Slightly volatile in steam.

$FeCl_3$: white turbidity changing first to red and then to violet: a precipitate of α-dinaphthol is formed.

Aryloxyacetic acid: prisms (alcohol), m.p. 191–192°; neut. equiv. 202.

Picrate: orange needles, m.p. 189°.

105° Catechol, $HO \cdot C_6H_4 \cdot OH$.

Sublimes in vacuo.

$FeCl_3$: emerald green (water or alcohol).

Dibenzoyl derivative: prisms, m.p. 84°.

111° Resorcinol, $HO \cdot C_6H_4 \cdot OH$.

$FeCl_3$: green (alcohol), violet (water).

Dibenzoate: prisms, m.p. 117°.

Bromination (acetic acid) ⟶ tribromoresorcinol, needles (water), m.p. 112°.

123° β-Naphthol, $C_{10}H_7 \cdot OH$.

Sublimes. Slightly volatile in steam.

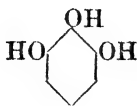
$FeCl_3$: faint green colour: the solution becomes turbid and finally deposits a ppt. of β-dinaphthol.

Benzoyl derivative: prisms, m.p. 107°.

Aryloxyacetic acid: prisms (aq. alcohol), m.p. 156°; neut. equiv. 202.

Picrate: orange needles, m.p. 156°.

m.p.

133° Pyrogallol, (structure: benzene ring with OH groups at 1, 2, 3 positions — HO, OH, OH)

Sublimes.

$FeCl_3$: green colour turning brown (alcohol); blue turning redish-brown (water).

Triacetate: hexagonal prisms, m.p. 163°.

172° Hydroquinone, $HO \cdot C_6H_4 \cdot OH$.

Sublimes.

$FeCl_3 \longrightarrow$ quinone: recognised by its pungent odour.

Dibenzoyl derivative: m.p. 199°.

218° Phloroglucinol, $C_6H_3 \begin{cases} OH\ (1). \\ OH\ (3). \\ OH\ (5). \end{cases}$

Sublimes.

$FeCl_3$: green colour (alcohol), transient violet on heating in water.

Tribenzoyl derivative: m.p. 173°.

Bromination (acetic acid) $\longrightarrow$ tribromo derivative, needles or prisms, m.p. 151°.

250° Phenolphthalein

H_2SO_4 gives red colour. Soluble in NaOH giving red colour.

Diacetyl derivative: octagonal plates, m.p. 143°.

Halogeno- and Nitro-Phenols

(General tests, see pp. 55–57. Colour tests, see p. 33)

Liquids

b.p.

176° *o*-Chlorophenol, $Cl \cdot C_6H_4 \cdot OH$, m.p. 7°.

$FeCl_3$: greenish-blue (alcohol), violet (water).

Nitration (fuming HNO_3 in acetic acid) $\longrightarrow$ 2-chloro-4 : 6-dinitrophenol, prisms (acetic acid), m.p. 113°.

Aryloxyacetic acid: prisms (aq. alcohol), m.p. 145°; neut. equiv. 186.

b.p.

194° *o*-Bromophenol, $C_6H_4<^{OH}_{Br}$

FeCl$_3$: violet (water), green (alcohol).

Nitration (fuming HNO$_3$ in acetic acid) $\longrightarrow$ 2-bromo-4 : 6-dinitrophenol, prisms (acetic acid), m.p. 118°.

Aryloxyacetic acid : prisms (aq. alcohol), m.p. 142°; neut. equiv. 231.

214° *m*-Chlorophenol, $Cl \cdot C_6H_4 \cdot OH$, m.p. 33°.

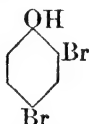
Benzoyl derivative : m.p. 71°.

Aryloxyacetic acid : prisms, m.p. 108–110°; neut. equiv. 186.

217° *p*-Chlorophenol, $Cl \cdot C_6H_4 \cdot OH$, m.p. 43°.

FeCl$_3$: violet (water), green (alcohol).

Benzoyl derivative : plates, m.p. 93°.

Nitration (fuming HNO$_3$ in acetic acid) $\longrightarrow$ 4-chloro-2 : 6-dinitrophenol, prisms (acetic acid), m.p. 81°.

Aryloxyacetic acid : prisms, m.p. 155–156°; neut. equiv. 186.

236° *m*-Bromophenol, $Br \cdot C_6H_4 \cdot OH$, m.p. 33°.

Aryloxyacetic acid : prisms, m.p. 108°; neut. equiv. 231.

Solids

m.p.

40° 2 : 4-Dibromophenol, [OH, Br, Br], b.p. 238°.

FeCl$_3$: yellowish-green (alcohol).

Benzoyl derivative : needles, m.p. 101°.

Nitration (fuming HNO$_3$ and acetic acid) $\longrightarrow$ 6-nitro-compound, prisms (acetic acid), m.p. 95°.

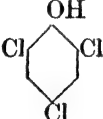
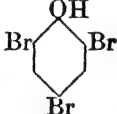
43° *p*-Chlorophenol. See liquids.

45° 2 : 4-Dichlorophenol, , b.p. 210°.

m.p.

Benzoyl derivative : m.p. 97°.
Nitration (fuming HNO_3 and acetic acid) ⟶ 6-nitro-compound, m.p. 122°.

45° *o*-Nitrophenol, $C_6H_4<^{OH}_{NO_2}$

Bright yellow.
$FeCl_3$: no colour.
Volatile in steam.
Nitration (H_2SO_4 and fuming HNO_3) ⟶ picric acid, yellow prisms, m.p. 122°.

64° *p*-Bromophenol, $Br\cdot C_6H_4\cdot OH$.
$FeCl_3$: violet (water).
Benzoyl derivative : m.p. 104°.
Nitration (fuming HNO_3 in acetic acid) ⟶ 4-bromo-2 : 6-dinitrophenol, yellow needles, m.p. 76°.
Aryloxyacetic acid : m.p. 157° : neut. equiv. 231.

67° *sym.*-Trichlorophenol,

$FeCl_3$: no colour.
Benzoyl derivative : m.p. 70°.

95° *sym.*-Tribromophenol,

$FeCl_3$: no colour.
Acetyl derivative : needles, m.p. 82°.

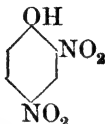
96° *m*-Nitrophenol, $NO_2\cdot C_6H_4\cdot OH$.
Pale yellow. Not volatile in steam.
$FeCl_3$: reddish-violet (water).
Benzoyl derivative : prisms, m.p. 95°.

114° *p*-Nitrophenol, $NO_2\cdot C_6H_4\cdot OH$.
Colourless. Not volatile in steam.
$FeCl_3$: violet-red (water); reddish-brown (alcohol).

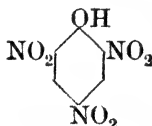
m.p.

Nitration (fuming HNO_3 and H_2SO_4) ⟶ picric acid, yellow prisms, m.p. 122°.

Benzoyl derivative: prisms, m.p. 142°.

114° 2 : 4-Dinitrophenol, (structure: OH at 1, NO_2 at 2 and 4)

Nitration (fuming HNO_3 and H_2SO_4) ⟶ picric acid, yellow prisms, m.p. 122°.

Molecular compound with naphthalene (benzene soln.), needles, m.p. 96°.

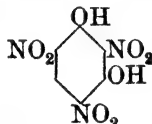
122° Picric acid,

Yellow.

A red colour is produced on boiling with aq. KCN.

Molecular compound with naphthalene: yellow needles, m.p. 149°.

138° 2 : 4-Dinitro-α-naphthol.

Yellow. Sodium salt is Martius Yellow.

174° 2 : 4 : 6-Trinitroresorcinol,

Yellow.

Forms double compounds with many aromatic hydrocarbons.

Methylamine salt: yellow prisms, m.p. 191°.

Ethers

(General tests, see p. 57)

Liquids

b.p.

35° Diethyl ether, $C_2H_5{\cdot}O{\cdot}C_2H_5$, d 0·7142.

Characteristic odour. Highly inflammable.

b.p.

124° Paraldehyde. See Aldehydes.

154° Anisole, $C_6H_5 \cdot O \cdot CH_3$, d 0·9942.

2 : 4-Dibromanisole: anisole is treated with bromine and the soln. after standing for 15 mins. is shaken with Na_2CO_3 soln. The ppt. so obtained is washed with water and crystallised from CH_3OH; prisms, m.p. 61°.

171° *o*-Cresyl methyl ether, $CH_3 \cdot C_6H_4 \cdot OCH_3$, d 0·981.

Bromination (acetic acid) ⟶ bromo-compound, plates, m.p. 64°.

172° Phenetole, $C_6H_5 \cdot O \cdot C_2H_5$, d 0·9651.

176° *p*-Cresyl methyl ether, $CH_3 \cdot C_6H_4 \cdot OCH_3$.

Oxidation ($KMnO_4$—1 hr.) ⟶ anisic acid, prisms, m.p. 184°.

177° *m*-Cresyl methyl ether, $CH_3 \cdot C_6H_4 \cdot OCH_3$.

Bromination (acetic acid) ⟶ tribromo-compound, needles (aq. CH_3OH), m.p. 85°.

Oxidation ($KMnO_4$—1 hr.) ⟶ *m*-methoxybenzoic acid, m.p. 106°.

196° Diethylene glycol monomethyl ether, d^{20}_{20} 1·023.

206° Veratrole, $C_6H_4(OCH_3)_2$, m.p. 22°.

Bromination (acetic acid) ⟶ dibromoveratrol, prisms, m.p. 91°.

214° Resorcinol dimethyl ether, $CH_3O \cdot C_6H_4 \cdot OCH_3$.

Bromination (acetic acid) ⟶ 4 : 6-dibromo-compound: cubic prisms, m.p. 141°.

218° *o*-Bromanisole, $CH_3O \cdot C_6H_4 \cdot Br$.

Bromination (see Anisole) ⟶ 2 : 4-dibromanisole, plates, m.p. 61°.

223° *p*-Bromanisole, $Br \cdot C_6H_4 \cdot OCH_3$.

Bromination (see Anisole) ⟶ 2 : 4-dibromanisole, plates, m.p. 61°.

Bromination as above for 2 hrs. ⟶ 2 : 4 : 6-tribromanisole, needles, m.p. 88°.

232° Safrole, d 1·096.

232° Butyl carbitol, d 0·957.

b.p.

235° Resorcinol diethyl ether, $C_6H_4(OC_2H_5)_2$.
Bromination (acetic acid) ⟶ 4 : 6-dibromo-compound, prisms, m.p. 101°.

243° Resorcinol monomethyl ether, $CH_3O{\cdot}C_6H_4{\cdot}OH$.
$FeCl_3$: green (alcohol), violet (water).
Bromination (acetic acid) ⟶ 2 : 4 : 6-tribromo-compound, needles, m.p. 104°.

252° Diphenyl ether, $C_6H_5{\cdot}O{\cdot}C_6H_5$, m.p. 28°.
Bromination (acetic acid) ⟶ dibromo-compound, plates, m.p. 54°.

277° *o*-Nitroanisole, $CH_3O{\cdot}C_6H_4{\cdot}NO_2$.
Bromination (see Anisole) ⟶ 4-bromo-compound, elongated prisms, m.p. 87°.

265° α-Naphthyl methyl ether, $C_{10}H_7{\cdot}OCH_3$.

Solids

m.p.

55° Hydroquinone dimethyl ether, $CH_3O{\cdot}C_6H_4{\cdot}OCH_3$.
Bromination (acetic acid) ⟶ dibromo-compound, prisms, m.p. 142°.
Green colour with H_2SO_4.

53° Hydroquinone monomethyl ether, $CH_3O{\cdot}C_6H_4{\cdot}OH$.
$FeCl_3$: green (water), green (alcohol).
Aryloxyacetic acid : m.p. 110°; neut. equiv. 182.

54° *p*-Nitroanisole, $NO_2{\cdot}C_6H_4{\cdot}OCH_3$.
Bromination (see Anisole) ⟶ 2-bromo-compound, needles, m.p. 106°.

72° Methyl β-naphthyl ether, $C_{10}H_7{\cdot}OCH_3$.

72° Hydroquinone diethyl ether, $C_2H_5O{\cdot}C_6H_4{\cdot}OC_2H_5$.
Bromination (acetic acid) ⟶ dibromo-compound, prisms, m.p. 142°.

CYCLIC ETHERS

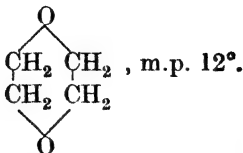
Liquids

b.p.

13° Ethylene oxide, $\begin{matrix}CH_2\\|\\CH_2\end{matrix}\!\!>O$
Sol. in water and organic solvents.

b.p.

Reduces silver nitrate.

101° 1 : 4-Dioxan, $O\begin{matrix} CH_2-CH_2 \\ CH_2-CH_2 \end{matrix}O$, m.p. 12°.

Volatile. Readily miscible with water and organic solvents.

Picrate : picric acid (1 g.) is dissolved in boiling dioxan (0·5 g.) and evaporated to dryness in a vacuum desiccator. The picrate is obtained as a pale yellow mass, m.p. 66°. Dissociates on crystallisation from alcohol.

Solid

m.p.

87° Diphenylene oxide, b.p. 288°.

Picrate : prepared in benzene soln., pale yellow crystals, m.p. 94°.

ALDEHYDES AND KETONES

(General tests, see pp. 58–61. Colour tests, see p. 46)

Liquids

b.p.

Gas Formaldehyde, H·CHO.

Generally obtained in 40% aq. soln. Characteristic pungent odour.

Dinitrophenylhydrazone : yellow elongated prisms, m.p. 166°.

21° Acetaldehyde, CH_3·CHO.

Characteristic odour. Miscible with water.

Positive iodoform test.

Dinitrophenylhydrazone : yellow prisms, m.p. 168°.

Semicarbazone : needles, m.p. 163°.

50° Propionaldehyde, CH_3·CH_2·CHO.

Pungent odour.

2 : 4-Dinitrophenylhydrazone : orange needles, m.p. 156°.

b.p.

53° Acrolein, $CH_2:CH \cdot CHO$.

Pungent odour. Polymerises readily, but can be stabilised by the presence of hydroquinone (1 part in 1000).

Dinitrophenylhydrazone : orange-red, m.p. 165°.

56° Acetone, $CH_3 \cdot CO \cdot CH_3$, d_4^{25} 0·7857.

Characteristic pleasant odour.

Positive iodoform test.

2 : 4-Dinitrophenylhydrazone : long, orange needles, m.p. 128°.

Semicarbazone : prisms (methyl alcohol), m.p. 187°.

75° *n*-Butyraldehyde, $CH_3 \cdot CH_2 \cdot CH_2 \cdot CHO$, d 0·817.

2 : 4-Dinitrophenylhydrazone : orange plates, m.p. 123°.

80° Methyl ethyl ketone, $CH_3 \cdot CO \cdot CH_2 \cdot CH_3$, d 0·805.

Positive iodoform test.

2 : 4-Dinitrophenylhydrazone : orange needles, m.p. 115°.

Semicarbazone : cubic prisms (methyl alcohol), m.p. 148°.

80°/20 mm. Aldol, $CH_3 \cdot CHOH \cdot CH_2 \cdot CHO$.

Syrupy liquid.

88° Diacetyl, $CH_3 \cdot CO \cdot CO \cdot CH_3$, d 0·975.

Yellowish-green liquid. Pungent odour.

Dinitrophenylhydrazone : orange prisms, m.p. above 300°.

Osazone : diacetyl and phenylhydrazine are mixed in acetic acid. The osazone soon separates as a pale yellow powder, m.p. 245°.

98° Chloral, $CCl_3 \cdot CHO$.

Pungent odour.

Chloral on heating with sodium hydroxide soln. yields chloroform, which is detected by its odour.

102° Diethyl ketone, $C_2H_5 \cdot CO \cdot C_2H_5$, d 0·814.

Dinitrophenylhydrazone : orange needles, m.p. 156°.

Semicarbazone : plates (methyl alcohol), m.p. 139°.

b.p.

102° Methyl *n*-propyl ketone, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$.
Positive iodoform test.
Dinitrophenylhydrazone: orange plates, m.p. 141°.

102° *n*-Valeraldehyde, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CHO$.
Dinitrophenylhydrazone: orange prisms, m.p. 104°.

104–105° Crotonaldehyde, $CH_3{\cdot}CH{:}CH{\cdot}CHO$.
Irritating odour.
Dinitrophenylhydrazone: needles, m.p. 190°.
Semicarbazone: plates (aq. methyl alcohol), m.p. 204°.

106° Pinacolone, $(CH_3)_3C{\cdot}CO{\cdot}CH_3$.
Odour of peppermint.
Iodoform test negative.
Dinitrophenylhydrazone: orange prisms, m.p. 125°.
Semicarbazone: needles, m.p. 160°.

124° Paraldehyde, $(C_2H_4O)_3$, m.p. 12°.
Does not show the usual aldehyde reactions. It is easily depolymerised by acids to give acetaldehyde, which is readily identified as the dinitrophenylhydrazone.

130° Mesityl oxide, $CH_3{\cdot}CO{\cdot}CH{:}C(CH_3)_2$.
Positive iodoform test.
Dinitrophenylhydrazone: red prisms (acetic acid), m.p. 203°.
Semicarbazone: plates, m.p. 164°.

131° Cyclopentanone, $\begin{matrix} CH_2-CH_2 \\ | \\ CH_2-CH_2 \end{matrix} > CO$

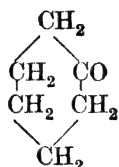
Dinitrophenylhydrazone: yellow prisms, m.p. 146°.
Semicarbazone: prisms (methyl alcohol), m.p. 215°.

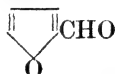
140° Acetylacetone, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_3$.
$FeCl_3$: intense red colour.
Positive iodoform test.
Dinitrophenylhydrazine $\longrightarrow$ 1-(2 : 4-dinitrophenyl)-3 : 5-dimethylpyrazole, pale yellow plates, m.p. 122°.

151° Methyl *n*-amyl ketone, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$.
Dinitrophenylhydrazone: orange plates, m.p. 67°.
Semicarbazone: elongated prisms, m.p. 127°.

b.p.

156° Cyclohexanone,

CH_2
CH_2 CO
CH_2 CH_2
CH_2

Dinitrophenylhydrazone: yellow prisms, m.p. 162°.
Semicarbazone: elongated prisms, m.p. 166°.

162° Furfural,

Odour similar to that of benzaldehyde. Colourless liquid turning brown on exposure to air.
Dinitrophenylhydrazone: reddish-brown needles, m.p. 202°.

166° Diacetone alcohol, $(CH_3)_2 \cdot C(OH) \cdot CH_2 \cdot CO \cdot CH_3$.
Dinitrophenylhydrazine ⟶ dinitrophenylhydrazone of mesityl oxide, red prisms (acetic acid), m.p. 203°.

172° Methyl hexyl ketone, $CH_3 \cdot CO \cdot (CH_2)_5CH_3$.
Dinitrophenylhydrazone: orange needles (methyl alcohol), m.p. 60°.

178° Benzaldehyde, $C_6H_5 \cdot CHO$.
Oil-of-bitter-almond odour. Does not reduce Fehling's soln. Volatile in steam.
Phenylhydrazone: plates, m.p. 156°.
Dinitrophenylhydrazone: orange needles (acetic acid), m.p. 237°.
Semicarbazone: needles (acetic acid), m.p. 222° (d).
Oxidation ($KMnO_4$—½ hr.) ⟶ benzoic acid, plates (water), m.p. 122°.

193° Phenylacetaldehyde, $C_6H_5 \cdot CH_2 \cdot CHO$.
Odour of hyacinths. Easily polymerised.
Dinitrophenylhydrazone: orange, m.p. 121°.

197° Salicylaldehyde, $HO \cdot C_6H_4 \cdot CHO$.
Pleasant odour. Assumes a blood-red colour on standing. Volatile in steam.
$FeCl_3$: blood-red (alcohol), violet (water).
Dinitrophenylhydrazone: red needles, m.p. 252° (d).

b.p.

Phenylhydrazone : plates, m.p. 143°.
Semicarbazone : needles or cubic prisms (acetic acid), m.p. 229°.
Bromination (acetic acid) ⟶ 5-bromo-2-hydroxybenzaldehyde, needles (aq. alcohol), m.p. 106°.

198° Phorone, $(CH_3)_2C{:}CH{\cdot}CO{\cdot}CH{:}C(CH_3)_2$, m.p. 28°.
Dinitrophenylhydrazone : elongated red prisms, m.p. 118°.
Semicarbazone : m.p. 186°.
Bromination (acetic acid) ⟶ tetrabromide, needles, m.p. 88°.

202° Acetophenone, $C_6H_5{\cdot}CO{\cdot}CH_3$, m.p. 20°.
Pleasant odour.
Positive iodoform reaction.
Dinitrophenylhydrazone : orange-red needles (acetic acid), m.p. 249°.
Phenylhydrazone : plates, m.p. 106°.
Semicarbazone : hexagonal plates, m.p. 203°.
Oxidation ($KMnO_4$—1 hr.) ⟶ benzoic acid, plates (water), m.p. 122°.

210° *l*-Menthone, $CH_3{\cdot}CH \lt \begin{matrix}CH_2-CH_2\\CH_2-CO\end{matrix} \gt CH{\cdot}CH(CH_3)_2$.
Odour of peppermint.
Dinitrophenylhydrazone : orange needles, m.p. 146°.
Semicarbazone : prisms, m.p. 189°.

234° Hydrocinnamaldehyde, $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}CHO$.
2 : 4-Dinitrophenylhydrazone : yellow needles, m.p. 149°.
Semicarbazone : plates, m.p. 127°.

232° *d*-Carvone, $CH_3{\cdot}C \lt \begin{matrix}CO-CH_2\\CH-CH_2\end{matrix} \gt CH{\cdot}C(CH_3){:}CH_2$.
Pleasant-smelling liquid.
Dinitrophenylhydrazone : red prisms, m.p. 189°.
Semicarbazone : prisms, m.p. 162°.

224° Pulegone, $CH_3{\cdot}CH \lt \begin{matrix}CH_2-CH_2\\CH_2-CO\end{matrix} \gt C{:}C(CH_3)_2$.
Odour of peppermint.

b.p.

Dinitrophenylhydrazone : red, rectangular plates, m.p. 147°.

225° *p*-Methylacetophenone, $CH_3 \cdot C_6H_4 \cdot CO \cdot CH_3$.

Positive iodoform test.

Dinitrophenylhydrazone : red prisms (acetic acid), m.p. 265°.

240° Propiophenone, $C_6H_5 \cdot CO \cdot CH_2 \cdot CH_3$.

Dinitrophenylhydrazone : orange-red plates (acetic acid), m.p. 191°.

Semicarbazone : needles, m.p. 174°.

247°. Anisaldehyde, $CH_3O \cdot C_6H_4 \cdot CHO(1:4)$.

Pleasant odour.

Dinitrophenylhydrazone : red plates (acetic acid), m.p. 253°.

Phenylhydrazone : plates, m.p. 120°.

Semicarbazone : prisms (acetic acid), m.p. 204°.

Oxidation ($KMnO_4$—1 hr.) ⟶ anisic acid, m.p. 184°.

250° Cinnamaldehyde, $C_6H_5 \cdot CH{:}CH \cdot CHO$.

Characteristic odour.

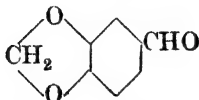
Dinitrophenylhydrazone : red plates (acetic acid), m.p. 248°.

Phenylhydrazone : plates, m.p. 170°.

Semicarbazone : needles (acetic acid), m.p. 215°.

Solids

m.p.

37° Piperonal,

Odour of heliotrope. Sublimes.

H_2SO_4 gives yellow coloration.

Dinitrophenylhydrazone : cubic prisms (xylene), m.p. 266°.

Phenylhydrazone : prisms, m.p. 100°.

Nitro derivative : piperonal (0·2 g.) is dissolved in 5 c.c. cold conc. HNO_3. On dilution with water the nitro compound is precipitated. Prisms, m.p. 97°.

m.p.

42° Benzalacetone, $C_6H_5 \cdot CH\colon CH \cdot CO \cdot CH_3$.

Conc. H_2SO_4 gives orange-red colour.

Positive iodoform test.

Dinitrophenylhydrazone : red needles (acetic acid), m.p. 227°.

Semicarbazone : needles or plates, m.p. 187°.

Bromination (CCl_4) $\longrightarrow$ dibromide, prisms, m.p. 125°.

48° Benzophenone, $C_6H_5 \cdot CO \cdot C_6H_5$.

Sublimes.

Dinitrophenylhydrazone : orange rhombic prisms (acetic acid), m.p. 238°.

Phenylhydrazone: needles, m.p. 137°.

Semicarbazone : needles, m.p. 167°.

58° Benzalacetophenone, $C_6H_5 \cdot CH\colon CH \cdot CO \cdot C_6H_5$.

H_2SO_4 gives deep yellow coloration.

Dinitrophenylhydrazone : orange needles (acetic acid), m.p. 248°.

Bromination (acetic acid) $\longrightarrow$ dibromide, prisms (acetic acid), m.p. 158°.

60° β-Naphthaldehyde, $C_{10}H_7 \cdot CHO$.

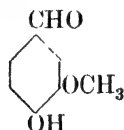
Dinitrophenylhydrazone : red needles (acetic acid), m.p. 270°.

Phenylhydrazone : plates, m.p. 217°.

60° Deoxybenzoin, $C_6H_5 \cdot CH_2 \cdot CO \cdot C_6H_5$.

Dinitrophenylhydrazone : orange needles, m.p. 195°.

Semicarbazone : needles, m.p. 148°.

81° Vanillin,

Odour of vanilla. Sublimes.

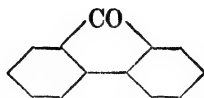
$FeCl_3$: blue (alcohol).

Dinitrophenylhydrazone : red needles (acetic acid), m.p. 275°.

Bromination (acetic acid) $\longrightarrow$ 5-bromovanillin, prisms (acetic acid), m.p. 164°.

m.p.

84° Fluorenone,

CO

Yellow. Slightly volatile in steam.
H_2SO_4 gives a violet coloration.
Phenylhydrazone : yellow needles, m.p. 151°.

95° Benzil, $C_6H_5 \cdot CO \cdot CO \cdot C_6H_5$.
Yellow.
Dinitrophenylhydrazone : orange needles, m.p. 189°.
o-Phenylenediamine ⟶ quinoxaline, needles, m.p. 124°.

108° *m*-Hydroxybenzaldehyde, $HO \cdot C_6H_4 \cdot CHO$.
Not volatile in steam.
$FeCl_3$: violet colour on warming in water.
Dinitrophenylhydrazone : red prisms, m.p. 260°.

112° Dibenzalacetone, $C_6H_5 \cdot CH{:}CH \cdot CO \cdot CH{:}CH \cdot C_6H_5$.
H_2SO_4 gives red coloration.
Dinitrophenylhydrazone : red plates, m.p. 180°.
Semicarbazone : needles (acetic acid), m.p. 187°.

117° *p*-Hydroxybenzaldehyde, $HO \cdot C_6H_4 \cdot CHO$.
Sublimes. Not volatile in steam.
$FeCl_3$: violet (water).
Phenylhydrazone : plates, m.p. 177°.
Semicarbazone : needles, m.p. 223°.
Bromination ⟶ 3 : 5-dibromo-4-hydroxybenzaldehyde, needles, m.p. 182°.

137° Benzoin, $C_6H_5 \cdot CHOH \cdot CO \cdot C_6H_5$.
Reduces Fehling's soln.
Dinitrophenylhydrazone : orange needles, m.p. 245°.
Acetate : plates, m.p. 83°.

172° Benzanthrone.
H_2SO_4 ⟶ red fluorescent soln.

179° *d*-Camphor.
Characteristic odour. Sublimes. Volatile in steam.
Dinitrophenylhydrazone (Brady's method) : orange prisms, m.p. 177°.

Halogeno- and Nitro-Carbonyl Compounds

(General tests, see pp. 58–61. Colour tests, see p. 46)

Liquids

b.p.

208° *o*-Chlorobenzaldehyde, $Cl{\cdot}C_6H_4{\cdot}CHO$, m.p. 11°.
Dinitrophenylhydrazone: orange prisms (acetic acid), m.p. 207°.
Oxidation ($KMnO_4$—½ hr.) ⟶ *o*-chlorobenzoic acid, needles (water), m.p. 142°.

213° *m*-Chlorobenzaldehyde, $Cl{\cdot}C_6H_4{\cdot}CHO$, m.p. 18°.
Dinitrophenylhydrazone: orange needles (acetic acid), m.p. 245°.
Oxidation ($KMnO_4$—½ hr.) ⟶ *m*-chlorobenzoic acid, prisms (aq. alcohol), m.p. 158°.

232° *p*-Chloracetophenone, $Cl{\cdot}C_6H_4{\cdot}CO{\cdot}CH_3$, m.p. 20°.
Positive iodoform reaction.
Phenylhydrazone: plates, m.p. 112°.
Dinitrophenylhydrazone: red crystals, m.p. 239°.
Oxidation ($KMnO_4$—1 hr.) ⟶ *p*-chlorobenzoic acid, needles (water), m.p. 243°.

Solids

m.p.

44° *o*-Nitrobenzaldehyde, $NO_2{\cdot}C_6H_4{\cdot}CHO$.
Phenylhydrazone: red hexagonal prisms, m.p. 157°.
Dinitrophenylhydrazone: yellow (acetic acid), m.p. 250°.

47° *p*-Chlorobenzaldehyde, $Cl{\cdot}C_6H_4{\cdot}CHO$.
Dinitrophenylhydrazone: orange needles (acetic acid), m.p. 265°.
Oxidation ($KMnO_4$—½ hr.) ⟶ *p*-chlorobenzoic acid, needles (water), m.p. 243°.

50° ω-Bromacetophenone, $C_6H_5{\cdot}CO{\cdot}CH_2Br$.
Irritating odour.
Oxidation ($KMnO_4$—1 hr.) ⟶ benzoic acid, plates (water), m.p. 122°.

m.p.

60° *p*-Bromacetophenone, $Br{\cdot}C_6H_4{\cdot}CO{\cdot}CH_3$.
Positive iodoform reaction.
Phenylhydrazone: plates, m.p. 126°.
Dinitrophenylhydrazone: orange prisms (acetic acid), m.p. 235°.
Oxidation ($KMnO_4$—1 hr.) ⟶ *p*-bromobenzoic acid, prisms (aq. alcohol), m.p. 254°.

58° *m*-Nitrobenzaldehyde, $NO_2{\cdot}C_6H_4{\cdot}CHO$.
Phenylhydrazone: orange prisms, m.p. 126°.
Dinitrophenylhydrazone: yellow prisms (acetic acid), m.p. 292°.
Oxidation ($KMnO_4$—½ hr.) ⟶ *m*-nitrobenzoic acid, m.p. 142°.

80° *m*-Nitroacetophenone, $NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}CH_3$.
Phenylhydrazone: red prisms, m.p. 135°.
Dinitrophenylhydrazone: orange needles (acetic acid), m.p. 228°.

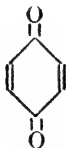
106° *p*-Nitrobenzaldehyde, $NO_2{\cdot}C_6H_4{\cdot}CHO$.
Phenylhydrazone: red prisms, m.p. 169°.
Dinitrophenylhydrazone: m.p. above 300°.
Oxidation ($KMnO_4$—½ hr.) ⟶ *p*-nitrobenzoic acid, plates (aq. alcohol), m.p. 242°.

109° *p*-Bromophenacyl bromide, $Br{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2Br$.
Oxidation ($KMnO_4$—1 hr.) ⟶ *p*-bromobenzoic acid, prisms (aq. alcohol), m.p. 254°.

125° *p*-Phenylphenacyl bromide, $C_6H_5{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2Br$.

Quinones

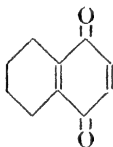
(General tests, see p. 61)

116° Benzoquinone,

Yellow. Sharp odour. Sublimes readily. Volatile in steam.

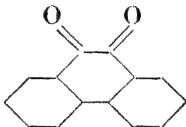
m.p.

Reduces ammoniacal $AgNO_3$.

On allowing quinone to stand in sulphurous acid solution over-night a clear soln. is obtained which on extraction with ether and evaporation yields hydroquinone, m.p. 172°.

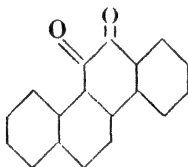
126° α-Naphthoquinone,

Yellow. Sublimes. Volatile in steam. Odour similar to that of quinone.

Semicarbazone: yellow needles (acetic acid), m.p. 247° (d).

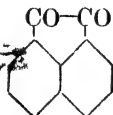
208° Phenanthraquinone,

Orange. Sublimes.

H_2SO_4 ⟶ green colour.

o-Phenylenediamine ⟶ quinoxaline, needles, m.p. 222°.

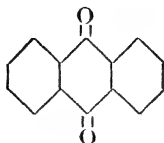
240° Chrysoquinone,

Red. Sublimes.

H_2SO_4 ⟶ bluish-violet colour.

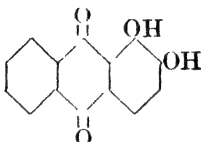
261° Acenaphthenequinone,

Yellow. Sublimes.

o-Phenylenediamine ⟶ quinoxaline, needles (acetic acid), m.p. 241°.

m.p.

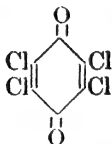
286° Anthraquinone,

Pale yellow. Sublimes. Not reduced by sulphurous acid.

Oxanthrol test : A pinch of the quinone is heated with a trace of zinc dust, 2 drops of caustic soda solution, and 2 c.c. water. A red colour is obtained which disappears on shaking. The colour reappears on heating.

289° Alizarin,

Orange-red.

H_2SO_4 gives deep red colour. NaOH gives violet colour.

Monoacetyl derivative : Alizarin (0·2 g.) is heated with acetic anhydride (2 c.c.) and acetyl chloride (0·2 c.c.) until a clear solution is obtained—about 4 hrs. On cooling, the monoacetyl derivative separates : yellow plates (acetic acid), m.p. 205°.

290° Chloranil (sealed tube)

Yellow colour. Sublimes.

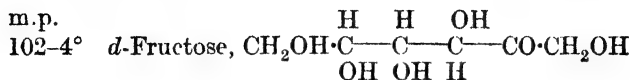
Phenylhydrazine compound : a suspension of chloranil in alcohol is treated with phenylhydrazine in the cold. A solution is obtained which on the addition of water yields the phenylhydrazine compound : plates (aq. alcohol), m.p. 239°.

Carbohydrates

(General tests, see pp. 61–64. Colour tests, see pp. 40–41. Osazones, see p. 88)

m.p.

102–4° *d*-Fructose,

$$CH_2OH\cdot\begin{matrix}H\\C\\OH\end{matrix}-\begin{matrix}H\\C\\OH\end{matrix}-\begin{matrix}OH\\C\\H\end{matrix}-CO\cdot CH_2OH$$

$[\alpha]_D^{20} = -133^\circ \longrightarrow -92^\circ$.

Reduces Fehling's soln.

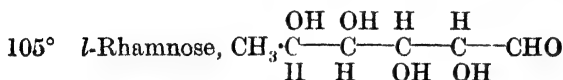
Osazone (formed in 2 min.): yellow needles, m.p. 204–205°.

Selenium dioxide test: the sugar on boiling with a little SeO_2 and dil. HCl gives a red ppt. of selenium in a few seconds. This test is not given by glucose, lactose, or maltose, and only on longer boiling by sucrose.

Seliwanoff's test: red colour.

Bredereck's test: a little fructose is dissolved in 10 c.c. water, and 10 c.c. of 4% ammonium molybdate and 4 drops acetic acid are added. A deep blue colour develops in a few minutes when the solution is heated in boiling water.

105° *l*-Rhamnose,

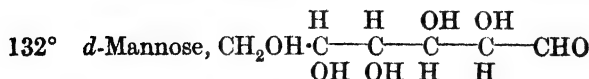
$$CH_3\cdot\begin{matrix}OH\\C\\H\end{matrix}-\begin{matrix}OH\\C\\H\end{matrix}-\begin{matrix}H\\C\\OH\end{matrix}-\begin{matrix}H\\C\\OH\end{matrix}-CHO$$

$[\alpha]_D^{20} = +9{\cdot}4^\circ$.

Reduces Fehling's soln.

Crystallises with 1 mol. water, m.p. 93–94°.

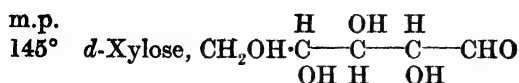
Osazone (formed in 7 min.): yellow needles, m.p. 182°.

132° *d*-Mannose,

$$CH_2OH\cdot\begin{matrix}H\\C\\OH\end{matrix}-\begin{matrix}H\\C\\OH\end{matrix}-\begin{matrix}OH\\C\\H\end{matrix}-\begin{matrix}OH\\C\\H\end{matrix}-CHO$$

$[\alpha]_D^{20} = -16{\cdot}3^\circ \longrightarrow +14{\cdot}5^\circ$.

Reduces Fehling's soln.

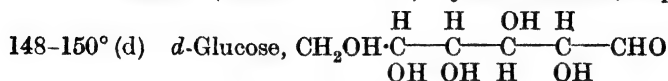
Phenylhydrazine $\longrightarrow$ phenylhydrazone (30 seconds), plates, m.p. 199–200° (d).

m.p.

145° *d*-Xylose, $CH_2OH\cdot\underset{OH}{\overset{H}{C}}-\underset{H}{\overset{OH}{C}}-\underset{OH}{\overset{H}{C}}-CHO$

$[\alpha]^{20}_{D} = +92° \longrightarrow +19°$.

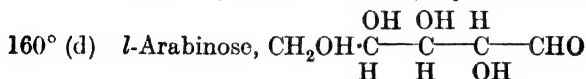
Reduces Fehling's soln.

Osazone (formed in 7 min.): yellow needles, m.p. 163°.

148–150° (d) *d*-Glucose, $CH_2OH\cdot\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-\underset{H}{\overset{OH}{C}}-\underset{OH}{\overset{H}{C}}-CHO$

$[\alpha]^{D}_{20} = +111{\cdot}2° \longrightarrow +52{\cdot}5°$.

Reduces Fehling's soln.

Osazone (formed in 5 min.): yellow needles, m.p. 205°.

160° (d) *l*-Arabinose, $CH_2OH\cdot\underset{H}{\overset{OH}{C}}-\underset{H}{\overset{OH}{C}}-\underset{OH}{\overset{H}{C}}-CHO$

$[\alpha]^{20}_{D} = +191° \longrightarrow +105{\cdot}5$.

Reduces Fehling's soln.

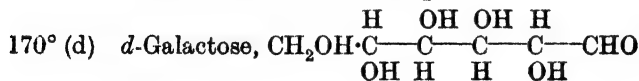
Osazone formed after 10 min. as an oil which goes solid: m.p. 165°.

160–165° (d) *d*-Maltose $C_{12}H_{22}O_{11}$ crystallises with 1 mol. water.

$[\alpha]^{20}_{D} = +118° \longrightarrow +136°$.

Reduces Fehling's soln.

Osazone. No ppt. is obtained until the soln. has been allowed to cool after heating in water-bath for 1·5 hrs. Yellow needles, m.p. 208°.

170° (d) *d*-Galactose, $CH_2OH\cdot\underset{OH}{\overset{H}{C}}-\underset{H}{\overset{OH}{C}}-\underset{H}{\overset{OH}{C}}-\underset{OH}{\overset{H}{C}}-CHO$

$[\alpha]^{20}_{D} = +140° \longrightarrow +81{\cdot}7°$.

Hydrated form, m.p. 118–120°.

Reduces Fehling's soln.

Osazone (formed in 19 min.): yellow needles, m.p. 186° (other values are also quoted).

Dil. $HNO_3 \longrightarrow$ mucic acid. Galactose (0·5 g.) in 10 c.c. HNO_3 (1·2) is evaporated to $\frac{1}{3}$ vol. on the water-bath. After 1 hr. mucic acid separates; m.p. 213°. On longer standing a good yield of the acid is obtained. Lactose also gives the acid.

m.p.

185° (d) Sucrose, $C_{12}H_{22}O_{11}$

$[\alpha]_D^{20} = +66{\cdot}5°$.

Does not reduce Fehling's soln. until hydrolysed with dil. HCl, when glucose and fructose are formed.

These are identified by osazone formation.

203° (d) Lactose, $C_{12}H_{22}O_{11}$, $[\alpha]_D^{20} = +83{\cdot}5° \longrightarrow +52{\cdot}5°$.

Occurs with 1 mol. water, which is lost at 130°.

Reduces Fehling's soln.

Osazone (formed after 1·5 hrs. and cooling): begins to melt at 200°.

Dil. $HNO_3 \longrightarrow$ mucic acid, m.p. 213° (cf. galactose).

d. Inulin, $[\alpha]_D^{20} = -40°$.

Insol. in cold water.

Does not reduce Fehling's soln.

No colour with iodine.

d. Glycogen, $[\alpha]_D^{20} = +196°$.

Like starch, it dissolves in water to give an opalescent soln. Does not reduce Fehling's soln.

Gives a reddish colour with iodine.

d. Starch.

Dissolves in boiling water to give an opalescent soln.

Blue colour with iodine.

225° (d) Cellobiose, $C_{12}H_{22}O_{11}$, $[\alpha] = +24{\cdot}4° \longrightarrow +35{\cdot}2°$.

Generally contains a little water.

Osazone: yellow needles, m.p. 198–200° (d).

Glycosides

(General tests, see p. 64)

166° α-Methylglucoside, $C_6H_{11}O_5{\cdot}OCH_3$, $[\alpha]_D^{20} = 158{\cdot}9°$ (water).

On boiling with dil. mineral acids yields CH_3OH and glucose.

163° Arbutin, $C_6H_4(O{\cdot}C_6H_{11}O_5)(OH)$ [benzene ring with $O{\cdot}C_6H_{11}O_5$ and OH para], $[\alpha]_D^{17} = -60{\cdot}34°$ (water).

Loses water at 110–115°.

m.p.

FeCl$_3$: violet colour.
On boiling with dil. mineral acids yields glucose and hydroquinone.

201° Salicin, $C_{13}H_{18}O_7$, $[\alpha]_D^{20} = -62{\cdot}56°$ (water).
Crimson colour with H_2SO_4.
FeCl$_3$: no colour unless salicin has previously been fused
Slowly hydrolysed to glucose and saligenin by dil. mineral acids.

214–216° Amygdalin, $C_{20}H_{27}O_{11}N$, $[\alpha]_D^{20} = -40{\cdot}57°$ (water).
Hot dil. HCl ⟶ glucose, benzaldehyde, and HCN.

Carboxylic Acids

(General tests, see pp. 65–66. Colour tests, see p. 44)

Liquids

b.p.

101° Formic acid, H·COOH.
Penetrating odour.
CO is evolved on heating with H_2SO_4.
2 c.c. $KMnO_4$ soln. heated with 5 drops H_2SO_4 and a few drops formic acid loses its colour.
Phenylhydrazide: plates, m.p. 145° (d).
Benziminazole picrate: orange needles, m.p. 230°.

118° Acetic acid, $CH_3{\cdot}COOH$, m.p. 17°.
Sharp odour. Hygroscopic.
Phenylhydrazide: plates, m.p. 129°.
p-Toluidide: plates, m.p. 147°.
2-Alkylbenziminazole picrate: yellow needles, m.p. 214°.

141° Propionic acid, $CH_3{\cdot}CH_2{\cdot}COOH$.
Sharp odour.
Phenylhydrazide: plates, m.p. 157°.
p-Toluidide: plates, m.p. 124°.
2-Alkylbenziminazole picrate: yellow plates, m.p. 120°.

155° *iso*Butyric acid, $(CH_3)_2CH{\cdot}COOH$.
Odour of rancid butter. Sol. in 5 parts cold water.
Phenylhydrazide: plates, m.p. 142°.
p-Toluidide: plates, m.p. 104°.
2-Alkylbenziminazole picrate: yellow plates, m.p. 136°.

b.p.

164° *n*-Butyric acid, $CH_3 \cdot CH_2 \cdot CH_2 \cdot COOH$.
Odour of rancid butter.
Phenylhydrazide: plates, m.p. 103° (d).
p-Toluidide: plates, m.p. 73°.
2-Alkylbenziminazole picrate: yellow plates, m.p. 124°.

165° (d) Pyruvic acid, $CH_3 \cdot CO \cdot COOH$, m.p. 14°.
Reduces ammoniacal $AgNO_3$.
Positive iodoform test.
Dinitrophenylhydrazone: yellow prisms, m.p. 218°.

186° *n*-Valeric acid, $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot COOH$.
Unpleasant odour.
p-Toluidide: plates, m.p. 74°.

205° *n*-Caproic acid, $CH_3 \cdot (CH_2)_4 \cdot COOH$.
Unpleasant odour.
p-Toluidide: plates, m.p. 73°.
Amide: plates, m.p. 100°.
Alkylbenziminazole picrate: yellow plates, m.p. 282°.

222–224° *n*-Heptylic acid, $CH_3(CH_2)_5 \cdot COOH$.
p-Toluidide: plates, m.p. 81°.
Amide: plates, m.p. 96°.

237° *n*-Caprylic acid, $CH_3 \cdot (CH_2)_6 \cdot COOH$, m.p. 16°.
p-Toluidide: plates, m.p. 70°.
Amide: plates, m.p. 110°.

250° Levulinic acid, $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot COOH$, m.p. 33°.
Positive iodoform test.
2 : 4-Dinitrophenylhydrazone: yellow needles ($CHCl_3$), m.p. 206°.

253° Pelargonic acid, $CH_3 \cdot (CH_2)_7 \cdot COOH$, m.p. 12°.
p-Toluidide: plates, m.p. 84°.
Amide: plates, m.p. 99°.

268–270° Capric acid, $CH_3 \cdot (CH_2)_8 \cdot COOH$, m.p. 31°.
Toluidide: plates, m.p. 78°.
Amide: plates, m.p. 108°.

285–286° Oleic acid, $CH_3 \cdot (CH_2)_7 \cdot CH{:}CH \cdot (CH_2)_7 \cdot COOH$.
p-Phenylphenacyl ester: m.p. 61°.

122°/ *dl*-Lactic acid, $CH_3 \cdot CHOH \cdot COOH$, m.p. 18°.
14 mm. Volatile in superheated steam.

b.p.

2-Alkylbenziminazole picrate: m.p. 131°.
p-Bromophenacyl ester: m.p. 113°.

Solids

m.p.

44° Lauric acid, $CH_3 \cdot (CH_2)_{10} \cdot COOH$.
Volatile in steam.
p-Toluidide: plates, m.p. 83°.
Amide: needles (water), m.p. 98°.

49° Hydrocinnamic acid, $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot COOH$.
Volatile in steam.
Oxidation ($KMnO_4$—½ hr.) ⟶ benzoic acid, plates (water), m.p. 122°.
p-Toluidide: prisms, m.p. 135°.

58° Myristic acid, $CH_3 \cdot (CH_2)_{12} \cdot COOH$.
p-Toluidide: plates, m.p. 93°.

62° Palmitic acid, $CH_3 \cdot (CH_2)_{14} \cdot COOH$.
Phenylhydrazide: plates, m.p. 111°.
p-Toluidide: plates, m.p. 96°.

66° Cyanacetic acid, $CN \cdot CH_2 \cdot COOH$.
See nitriles.

72° Stearic acid, $CH_3 \cdot (CH_2)_{16} \cdot COOH$.
Phenylhydrazide: plates, m.p. 112–115°.

72° α-Crotonic acid, $\begin{matrix} CH_3 \cdot CH \\ \| \\ HC \cdot COOH. \end{matrix}$
Reduces amm. $AgNO_3$ on warming.
Bromination (bromine) ⟶ α : β-dibromobutyric acid, prisms, (ligroin), m.p. 87°.

78° Phenylacetic acid, $C_6H_5 \cdot CH_2 \cdot COOH$.
p-Toluidide: plates, m.p. 133°.
Phenylhydrazide: needles, m.p. 175°.
p-Nitrobenzyl ester: needles, m.p. 65°.

80° Glycollic acid, $CH_2OH \cdot COOH$
Benziminazole picrate: yellow needles, m.p. 214°.

97° Glutaric acid, $COOH \cdot (CH_2)_3 \cdot COOH$.
p-Toluidide: hexagonal prisms, m.p. 217°.

m.p.

Di-phenylhydrazide : plates (acetic acid), m.p. 219°.
p-Nitrobenzyl ester : m.p. 69°.

100° *l*-Malic acid, $COOH{\cdot}CH_2{\cdot}CHOH{\cdot}COOH$.
p-Nitrobenzyl ester : m.p. 124°.

101° Oxalic acid—hydrated.

107° *o*-Toluic acid, $CH_3{\cdot}C_6H_4{\cdot}COOH$.
Volatile in steam.
Nitration (conc. H_2SO_4 and fuming HNO_3) ⟶ 3 : 5-dinitro-2-methylbenzoic acid, prisms, m p. 207°.
p-Toluidide : plates (aq. alcohol), m.p 158°.
Amide : plates (water), m.p. 142°.
p-Nitrobenzyl ester : m.p. 91°.

107° Azelaic acid, $COOH{\cdot}(CH_2)_7{\cdot}COOH$.
Diamide : prisms, m.p. 175°.

106° Pimelic acid, $COOH{\cdot}(CH_2)_5{\cdot}COOH$.
Sublimes.

112° *m*-Toluic acid, $CH_3{\cdot}C_6H_4{\cdot}COOH$.
Volatile in steam. Sublimes.
p-Toluidide : prisms, m.p. 118°.
Amide : needles (water), m.p. 97°.
p-Nitrobenzyl ester : m.p. 87°.

120° Mandelic acid, $C_6H_5{\cdot}CHOH{\cdot}COOH$.
Oxidation ($KMnO_4$—$\frac{1}{2}$ hr.) ⟶ benzoic acid, plates (water), m.p. 122°.
p-Toluidide : plates, m.p. 172°.
Methyl ester : sol. in water : prisms (ligroin), m.p. 56°.
Alkylbenziminazole picrate : yellow needles, m.p. 209°.

122° Benzoic acid, $C_6H_5{\cdot}COOH$.
Sublimes. Volatile in steam.
p-Toluidide : plates (aq. alcohol), m.p. 158°.
Amide : prisms (water), m.p. 130°.
p-Nitrobenzyl ester : m.p. 89°.

133° Maleic acid, $\begin{matrix} H{\cdot}C{\cdot}COOH \\ \| \\ H{\cdot}C{\cdot}COOH \end{matrix}$

Bromine (acetic acid) ⟶ fumaric acid.
p-Nitrobenzyl ester : m.p. 89°.

m.p.

136° Malonic acid, $COOH \cdot CH_2 \cdot COOH$.
(d) Di-*p*-toluidide : m.p. 250°.
p-Nitrobenzyl ester : m.p. 85°.

137° Cinnamic acid, $C_6H_5 \cdot CH{:}CH \cdot COOH$
On warming gently with H_2SO_4 a green and then a brownish-red colour is obtained.
Nitration (heating with fuming HNO_3 for 30 mins.) $\longrightarrow$ *p*-nitrobenzoic acid, prisms (acetic acid), m.p. 242°.
Bromination (CCl_4) $\longrightarrow$ α : β-dibromophenylpropionic acid, m.p. 201°. Bromination in acetic acid requires 24 hrs. for completion.
p-Toluidide : prisms, m.p. 168°.
Amide : needles (water), m.p. 148°.

145° Diphenylacetic acid, $(C_6H_5)_2CH \cdot COOH$.
Amide : cubic prisms, m.p. 167°.

150° Benzilic acid, $(C_6H_5)_2C{<}^{OH}_{COOH}$.
Conc. H_2SO_4 gives red colour.
Reduction $\longrightarrow$ diphenylacetic acid. Benzilic acid (0·5 g.), red phosphorus (0·1 g.), iodine (0·05 g.), and water (20 c.c.) are refluxed for 2 hrs. and filtered. The filtrate on cooling deposits diphenylacetic acid : prisms (aq. alcohol), m.p. 145°. Mixed m.p. is necessary : cf. m.p. of benzilic acid.
p-Nitrobenzyl ester : needles, m.p. 99°.

151° Adipic acid, $COOH \cdot (CH_2)_4 \cdot COOH$.
Sublimes.
p-Toluidide : needles, m.p. 238°.
Phenylhydrazide : plates (acetic acid), m.p. 206°.
Diamide : powder (water), m.p. 220°.
p-Nitrobenzyl ester : needles, m.p. 106°.

153° Citric acid, $COOH \cdot CH_2 \cdot C(OH)(COOH) \cdot CH_2 \cdot COOH$.
Contains 1 mol. water of crystallisation, which is lost at 130°.
Positive iodoform test.
p-Nitrobenzyl ester : m.p. 102°.

m.p.

159° Salicylic acid, $OH\cdot C_6H_4\cdot COOH$.
Sublimes. Volatile in steam.
$FeCl_3$: violet (water).
Nitration ⟶ 5-nitro-2-hydroxybenzoic acid. The acid (0·1 g.) is boiled for 1 min. with water (5 c.c.) and conc. HNO_3 (0·5 g.). The soln. is poured into water, and the ppt. crystallised from aq. alcohol. Needles, m.p. 227°.

162° α-Naphthoic acid, $C_{10}H_7\cdot COOH$.
Amide: plates (alcohol), m.p. 205°.

170° *d*- or *l*-Tartaric acid, $COOH\cdot \overset{OH}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}\cdot COOH$.
Fenton's test. A drop of $FeSO_4$ soln. and several drops of 3% H_2O_2 soln. are added to an aqueous soln. of the acid. A violet coloration is obtained by the addition of sodium hydroxide soln. Citric and malic acids do not give the coloration.
p-Toluidide: hexagonal prisms, m.p. 264°.
Phenylhydrazide: plates, m.p. about 240° (quick heating).

178° *p*-Toluic acid, $CH_3\cdot C_6H_4\cdot COOH$.
Sublimes. Volatile in steam.
Amide: prisms (water), m.p. 158°.
p-Toluidide: needles (aq. alcohol), m.p. 161°.
p-Nitrobenzyl ester: m.p. 104°.

184° Anisic acid, $CH_3O\cdot C_6H_4\cdot COOH(1:4)$.
Amide: plates, m.p. 162°.
p-Toluidide: prisms, m.p. 186°.
p-Nitrobenzyl ester: m.p. 132°.

186° β-Naphthoic acid, $C_{10}H_7\cdot COOH$.
Amide: plates (alcohol), m.p. 195°.
p-Toluidide: needles, m.p. 197°.

187° *d*-Camphoric acid, $C_{10}H_{16}O_4$.
With conc. H_2SO_4 on warming gives off CO.
Anhydride: the acid (1 g.) is heated for 30 mins. with

m.p.

acetyl chloride (3 c.c.) and acetic anhydride (3 c.c.). A ppt. is obtained by pouring the soln. into water. Prisms, m.p. 221°.

188° Succinic acid, $COOH \cdot CH_2 \cdot CH_2 \cdot COOH$.
p-Toluidide: prisms, m.p. 255°.
p-Nitrobenzyl ester: m.p. 88°.

198° (d) *trans*-Aconitic acid, $H \cdot C \cdot COOH$ / $COOH \cdot C \cdot CH_2 \cdot COOH$ (double bond between the two C atoms)
M.p. depends on rate of heating.
p-Nitrobenzyl ester: m.p. 76°.

195° (approx.) Phthalic acid, $COOH \cdot C_6H_4 \cdot COOH$.
The melting point is dependent on the rate of heating. On quick heating the m.p. is 231°.
Fluorescein test.
p-Toluidide: m.p. 201°.
Aniline salt: prepared in alcohol soln.—plates, m.p. 155°.
p-Nitrobenzyl ester: m.p. 155°.

201° *m*-Hydroxybenzoic acid, $HO \cdot C_6H_4 \cdot COOH$.
Sublimes. No colour with $FeCl_3$.
Acetyl derivative: plates (water), m.p. 130°.
Amide: plates, m.p. 170°.
p-Nitrobenzyl ester: m.p. 106°.

205–206° *dl*-Tartaric acid, $C_4H_6O_6$.
p-Nitrobenzyl ester: m.p. 163°.

206° Mucic acid, $COOH \cdot (CHOH)_4 \cdot COOH$.
Melting point depends on rate of heating. Slow heating, m.p. 206°; quick heating, m.p. 213°.
Tetra-acetyl derivative: needles (aq. alcohol), m.p. 266°.

213° *p*-Hydroxybenzoic acid, $HO \cdot C_6H_4 \cdot COOH$.
$FeCl_3$: no colour.
Acetyl derivative: cubic prisms (aq. alcohol), m.p. 185°.
Nitration (fuming HNO_3 and H_2SO_4) — → picric acid yellow plates (water), m.p. 122°.
Bromination (acetic acid) ⟶ 3 : 5-dibromo-4-hydroxybenzoic acid, elongated prisms (water), m.p. 270°.

m.p.

239° Gallic acid.

M.p. 239° if crystallised from water; otherwise the m.p. is 263°.

$FeCl_3$: black ppt. (water).

KCN soln.: brilliant red colour, which disappears if the soln. is allowed to stand for some minutes, but which reappears on shaking.

Formaldehyde test: a little of the acid is dissolved in dil. HCl and a few drops of formaldehyde are added. On cooling a condensation product in the form of needles separates.

286° (sealed tube) Fumaric acid, $COOH{\cdot}C{\cdot}H \atop H{\cdot}C{\cdot}COOH$ (double bond between the C atoms)

Sublimes.

p-Nitrobenzyl ester: m.p. 151°.

349° Isophthalic acid, $COOH{\cdot}C_6H_4{\cdot}COOH(1:3)$.

Sublimes.

Dimethyl ester: needles (aq. alcohol), m.p. 68°.

Diamide: prisms (acetic acid), m.p. 280°.

Subl. Terephthalic acid, $COOH{\cdot}C_6H_4{\cdot}COOH(1:4)$.

Dimethyl ester: plates, m.p. 140°.

p-Nitrobenzyl ester: m.p. 263°.

Halogeno- and Nitro-Carboxylic Acid

(General tests, see pp. 65–67)

Liquids

b.p.

190° Dichloracetic acid, $CHCl_2{\cdot}COOH$.

Aniline salt: plates, m.p. 122°.

Solids

m.p.

50° Bromacetic acid, $CH_2Br{\cdot}COOH$.

p-Nitrobenzyl ester: m.p. 88°.

57° Trichloracetic acid, $CCl_3{\cdot}COOH$.

Characteristic odour.

m.p.

Aniline salt: needles (benzene), m.p. 155°.
p-Nitrobenzyl ester: m.p. 80°.

63° Chloracetic acid, $CH_2Cl \cdot COOH$.
Sharp odour.
Aniline salt: needles (benzene), m.p. 94°.

142° *o*-Chlorobenzoic acid, $COOH \cdot C_6H_4 \cdot Cl$.
Sublimes.
Nitration (fuming HNO_3—30 sec.) ⟶ 2-chloro-5-nitrobenzoic acid, prisms (aq. alcohol), m.p. 160°.
Amide: prisms (water), m.p. 142°.
p-Nitrobenzyl ester: m.p. 106°.

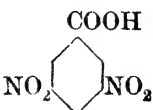
142° *m*-Nitrobenzoic acid, $NO_2 \cdot C_6H_4 \cdot COOH$.
Methyl ester: prisms, m.p. 78°.
Amide: prisms (aq. alcohol), m.p. 142°.
p-Nitrobenzyl ester: m.p. 141°.

147° *o*-Nitrobenzoic acid, $COOH \cdot C_6H_4 \cdot NO_2$.
Amide: prisms (aq. alcohol), m.p. 176°.
p-Nitrobenzyl ester: 112°.

150° *o*-Bromobenzoic acid, $COOH \cdot C_6H_4 \cdot Br$.
Sublimes.
Nitration (fuming HNO_3—30 sec.) ⟶ 2-bromo-5-nitrobenzoic acid, needles (water), m.p. 180°.
Amide: prisms (aq. alcohol), m.p. 157°.
p-Nitrobenzyl ester: m.p. 110°.

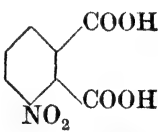
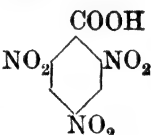
155° *m*-Bromobenzoic acid, $Br \cdot C_6H_4 \cdot COOH$.
Amide: prisms (water), m.p. 155°.
p-Nitrobenzyl ester: m.p. 105°.

158° *m*-Chlorobenzoic acid, $Cl \cdot C_6H_4 \cdot COOH$.
Amide: needles (water), m.p. 134°.
p-Nitrobenzyl ester: m.p. 107°.

162° *o*-Iodobenzoic acid, $COOH \cdot C_6H_4 \cdot I$.
Amide: prisms (aq. alcohol), m.p. 185°.
p-Nitrobenzyl ester: m.p. 111°.

181° 2 : 4-Dinitrobenzoic acid, $C_6H_3 \begin{cases} COOH & (1). \\ NO_2 & (2). \\ NO_2 & (4). \end{cases}$

Methyl ester: needles, m.p. 70°.

m.p.

Amide: needles (water), m.p. 203°.
p-Nitrobenzyl ester: m.p. 142°.

204° 3 · 5-Dinitrobenzoic acid, (ring formula: COOH with NO_2 at positions 3 and 5)

Methyl ester: 107°.
Amide: plates, m.p. 183°.
p-Nitrobenzyl ester: m.p. 157°.

218° (sealed tube) 3-Nitrophthalic acid, (ring formula: two COOH groups with NO_2 adjacent)

p-Nitrobenzyl ester: m.p. 189°.

220° 2 : 4 : 6-Trinitrobenzoic acid, (ring formula: COOH with three NO_2 groups)

Red colour with caustic soda soln.
On heating an aq. soln. of the sodium salt CO_2 is lost and 1 : 3 : 5-trinitrobenzene separates: m.p. 122°.

242° *p*-Nitrobenzoic acid, $NO_2 \cdot C_6H_4 \cdot COOH$.
Methyl ester: m.p. 96°.
Amide: cubic prisms, m.p. 201°.
p-Toluidide: needles (acetic acid), m.p. 203°.
p-Nitrobenzyl ester: m.p. 168°.

243° *p*-Chlorobenzoic acid, $Cl \cdot C_6H_4 \cdot COOH$.
Sublimes.
Amide: plates (water), m.p. 179°.
p-Nitrobenzyl ester: m.p. 129°.
Nitration (fuming HNO_3—30 sec.) ⟶ 4-chloro-3-nitrobenzoic acid, prisms, m.p. 180°.

254° *p*-Bromobenzoic acid, $Br \cdot C_6H_4 \cdot COOH$.
Nitration (fuming HNO_3—30 sec.) ⟶ 4-bromo-3-nitrobenzoic acid, prisms, m.p. 200°.
Methyl ester: needles, m.p. 81°.

m.p.

Amide: plates (water), m.p. 189°.
p-Nitrobenzyl ester: m.p. 139°.

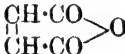
270° *p*-Iodobenzoic acid, $I{\cdot}C_6H_4{\cdot}COOH$.
Sublimes.
Methyl ester: needles (methyl alcohol), m.p. 114°.
Amide: plates (water), m.p. 217°.
p-Nitrobenzyl ester: m.p. 141°.

Acid Anhydrides

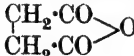
(General tests, see pp. 66–67)

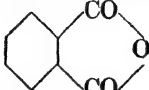
Liquids

b.p.

140° Acetic anhydride, $CH_3{\cdot}CO{\cdot}O{\cdot}CO{\cdot}CH_3$.
Pungent odour.
p-Toluidide: plates, m.p. 147°.

168° Propionic anhydride, $C_2H_5{\cdot}CO{\cdot}O{\cdot}CO{\cdot}C_2H_5$.
p-Toluidide: plates, m.p. 124°.

Solids

m.p.

44° Benzoic anhydride, $C_6H_5{\cdot}CO{\cdot}O{\cdot}CO{\cdot}C_6H_5$.
p-Toluidide: elongated prisms, m.p. 158°.

45° Chloracetic anhydride, $CH_2Cl{\cdot}CO{\cdot}O{\cdot}CO{\cdot}CH_2Cl$.
Anilide: m.p. 134°.

52° Maleic anhydride, $\begin{matrix} CH{\cdot}CO \\ \| \\ CH{\cdot}CO \end{matrix}\!\!>\!O$
Sublimes.
Anilic acid: yellow octahedra (acetone), m.p. 205°.

130° Succinic anhydride, $\begin{matrix} CH_2{\cdot}CO \\ | \\ CH_2{\cdot}CO \end{matrix}\!\!>\!O$
Anilic acid: yellow prisms (acetone), m.p. 147°.
p-Toluidide: prisms, m.p. 255°.

131° Phthalic anhydride, $C_6H_4\begin{matrix} CO \\ CO \end{matrix}\!\!>\!O$
Anilic acid: diamond-shaped prisms, m.p. 167°.
p-Toluidide: needles, m.p. 201°

m.p.

221° *d*-Camphoric anhydride.
Anilic acid: elongated prisms (acetone), m.p. 219°.

272° Naphthalic anhydride.
Gives with *o*-phenylenediamine a benziminazole derivative in acetic acid soln., pale yellow, m.p. 206°.

Esters

(General reactions, see p. 67)

Liquids

b.p.

32° Methyl formate, $H \cdot CO \cdot OCH_3$, d 0·975.
H_2SO_4 (warming) $\longrightarrow$ CO.
Formyl phenylhydrazide: plates, m.p. 145°.

54° Ethyl formate, $H \cdot CO \cdot OC_2H_5$, d 0·906.
H_2SO_4 (warming) $\longrightarrow$ CO.
Formyl phenylhydrazide: plates, m.p. 145°.

57° Methyl acetate, $CH_3 \cdot CO \cdot OCH_3$, d 0·933.
2-Alkylbenziminazole picrate: yellow needles, m.p. 214°.

77° Ethyl acetate, $CH_3 \cdot CO \cdot OC_2H_5$, d 0·899.
2-Alkylbenziminazole picrate: yellow needles, m.p. 214°.

142° *iso*Amylacetate, $CH_3 \cdot CO \cdot OCH_2 \cdot CH_2 \cdot CH(CH_3)_2$, d_4^{15} 0·8762.
Odour of banana.

145° Methyl *dl*-lactate, $CH_3 \cdot CHOH \cdot CO \cdot OCH_3$, d_4^{19} 1·0898.
Positive iodoform test.

155° Ethyl *dl*-lactate, $CH_3 \cdot CHOH \cdot CO \cdot OC_2H_5$, d_4^{19} 1·0308.
Positive iodoform test.

169° Methyl acetoacetate, $CH_3 \cdot CO \cdot CH_2 \cdot CO \cdot OCH_3$, d^{15} 1·081.
Dinitrophenylhydrazone: yellow plates, m.p. 110°.

181° Dimethyl malonate, $CH_2{<}{CO \cdot OCH_3 \atop CO \cdot OCH_3}$, d 1·1527.
Hydrazide: plates, m.p. 154°.
Decolorises bromine in the cold.

181° Ethyl acetoacetate,
$CH_3 \cdot CO \cdot CH_2 \cdot CO \cdot OC_2H_5 \rightleftarrows CH_3 \cdot C(OH){:}CH \cdot CO \cdot OC_2H_5$, d 1·025
Dinitrophenylhydrazone: orange needles, m.p. 96°.

b.p.

186° Diethyl oxalate, $C_2H_5O\cdot CO\cdot CO\cdot OC_2H_5$.
    H_2SO_4 (warming) $\longrightarrow$ $CO + CO_2$.
    Ammonia $\longrightarrow$ oxamide.
    Hydrazide : plates, m.p. 243°.

195° Dimethyl succinate, $\begin{array}{l}CH_2\cdot CO\cdot OCH_3\\ \vert \\ CH_2\cdot CO\cdot OCH_3\end{array}$
    Hydrazide : m.p. 168°.

196° Phenyl acetate, $CH_3\cdot CO\cdot O\cdot C_6H_5$, d_4^{15} 1·081.

196° Methyl levulinate, $CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CO\cdot OCH_3$, d 1·0474.
    Dinitrophenylhydrazone : yellow needles, m.p. 141°.

199° Diethyl malonate, $CH_2 < \begin{array}{l}CO\cdot OC_2H_5\\ CO\cdot OC_2H_5\end{array}$, d 1·0550.
    Decolorises bromine in the cold.
    Hydrazide : plates, m.p. 154°.

200° Methyl benzoate, $C_6H_5\cdot CO\cdot OCH_3$, d 1·103.
    Hydrolysis (NaOH) $\longrightarrow$ benzoic acid, plates (water), m.p. 122°.

206° Ethyl levulinate, $CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CO\cdot OC_2H_5$, d 1·0114.
    Dinitrophenylhydrazone : yellow needles, m.p. 101°.

213° Ethyl benzoate, $C_6H_5\cdot CO\cdot OC_2H_5$, d 1·066.
    Hydrolysis (NaOH) $\longrightarrow$ benzoic acid, plates (water), m.p. 122°.

217° Diethyl succinate, $C_2H_5O\cdot CO\cdot CH_2\cdot CH_2\cdot CO\cdot OC_2H_5$ d 1·0398.
    Hydrazide : plates, m.p. 167°.

218° *iso*Propyl benzoate, $C_6H_5\cdot CO\cdot O\cdot CH(CH_3)_2$ d 1·023.
    Hydrolysis (NaOH) $\longrightarrow$ benzoic acid, plates (water), m.p. 122°.

Methyl phenylacetate, $C_6H_5\cdot CH_2\cdot CO\cdot OCH_3$.
    Hydrolysis (NaOH) $\longrightarrow$ phenylacetic acid, plates (water), m.p. 78°.

224° Methyl salicylate, $HO\cdot C_6H_4\cdot COOCH_3$, d_{15}^{15} 1·189.
    Odour of oil of wintergreen.
    Hydrolysis (NaOH) $\longrightarrow$ salicylic acid, needles (water), m.p. 159°.

229° Ethyl phenylacetate, $C_6H_5\cdot CH_2\cdot CO\cdot OC_2H_5$, d_{15}^{15} 1·046.
    Hydrolysis (NaOH) $\longrightarrow$ phenylacetic acid, plates (water), m.p. 78°.

b.p.

230° Propyl benzoate, $C_6H_5 \cdot CO \cdot OC_3H_7$, d^{15} 1·032.
Hydrolysis (NaOH) ⟶ benzoic acid, plates (water), m.p. 122°.

234° Ethyl salicylate, $HO \cdot C_6H_4 \cdot COOC_2H_5$.
Odour of oil of wintergreen.
Hydrolysis (NaOH) ⟶ salicylic acid, needles (water), m.p. 159°.

258° Glyceryl triacetate, d_4^{15} 1·161.

271° Ethyl cinnamate, $C_6H_5 \cdot CH{:}CH \cdot CO \cdot OC_2H_5$, d 1·050, m.p. 12°.
Hydrolysis (NaOH) ⟶ cinnamic acid, plates (water), m.p. 137°.

280° Ethyl *d*-tartrate, d 1·206.

284° Dimethyl phthalate, $C_6H_4(COOCH_3)_2$.
Hydrolysis (NaOH) ⟶ phthalic acid, identified as aniline salt, plates, m.p. 155°.

294° Triethyl citrate, d 1·137.

298° Diethyl phthalate, $C_6H_4(COOC_2H_5)_2$.
Hydrolysis (NaOH) ⟶ phthalic acid, identified as the aniline salt, plates, m.p. 155°.

302° Diethyl isophthalate, $C_6H_4(COOC_2H_5)_2$.
Hydrolysis (NaOH) ⟶ isophthalic acid, identified as the dimethyl ester, needles, m.p. 68°.

341° Dibutyl phthalate, $C_6H_4(COOC_4H_9)_2$.
Hydrolysis (NaOH) ⟶ phthalic acid, identified as the aniline salt, plates, m.p. 155°.

Solids

m.p.

36° Methyl cinnamate, $C_6H_5 \cdot CH{:}CH \cdot CO \cdot OCH_3$.
Hydrolysis (NaOH) ⟶ cinnamic acid, plates (water), m.p. 137°.

39° Benzyl cinnamate, $C_6H_5 \cdot CH{:}CH \cdot CO \cdot OCH_2 \cdot C_6H_5$.
Hydrolysis (NaOH) ⟶ cinnamic acid, plates (water), m.p. 137°.

42° Phenyl salicylate, $HO \cdot C_6H_4 \cdot COOC_6H_5$.
No colour with $FeCl_3$.
Benzoyl derivative: m.p. 80°.

m.p.

44° Diethyl terephthalate, $C_6H_4(COOC_2H_5)_2$.
Hydrolysis (NaOH) ⟶ terephthalic acid, identified as methyl ester, plates m.p. 140°.

47° Ethyl *m*-nitrobenzoate, $NO_2 \cdot C_6H_4 \cdot COOC_2H_5$.
Hydrolysis (NaOH) ⟶ *m*-nitrobenzoic acid, needles (water), m.p. 142°.

54° Dimethyl oxalate, $CH_3O \cdot CO \cdot CO \cdot OCH_3$.
H_2SO_4 (warming) ⟶ $CO + CO_2$.
NH_3 ⟶ oxamide.
Hydrazide: plates, m.p. 243°.

57° Ethyl *p*-nitrobenzoate, $NO_2 \cdot C_6H_4 \cdot COOC_2H_5$.
Hydrolysis (NaOH) ⟶ *p*-nitrobenzoic acid, plates (aq. alcohol), m.p. 242°.

58° Methyl *d*-mandelate, $C_6H_5 \cdot CHOH \cdot CO \cdot OCH_3$.

67° Dimethyl isophthalate, $C_6H_4(COOCH_3)_2$ (1 : 3).
Hydrolysis (NaOH) ⟶ isophthalic acid, identified as the dimethyl ester, needles (aq. alcohol), m.p. 68°.

68° Phenyl benzoate, $C_6H_5 \cdot CO \cdot OC_6H_5$.
Hydrolysis (NaOH) ⟶ benzoic acid, plates (water), m.p. 122°.

78° Methyl *m*-nitrobenzoate, $NO_2 \cdot C_6H_4 \cdot COOCH_3$.
Hydrolysis (NaOH) ⟶ *m*-nitrobenzoic acid, needles (water), m.p. 142°.

96° Methyl *p*-nitrobenzoate, $NO_2 \cdot C_6H_4 \cdot COOCH_3$.
Hydrolysis (NaOH) ⟶ *p*-nitrobenzoic acid, plates (aq. alcohol), m.p. 242°.

140° Dimethyl terephthalate, $C_6H_4(COOCH_3)_2$ (1 : 4).
Hydrolysis (NaOH) ⟶ terephthalic acid, identified as *p*-nitrobenzyl ester, m.p. 263°.

Esters of Inorganic Acids. Nitrites, Nitrates, and Sulphates

(General tests, see p. 67)

Liquids

b.p.

Gas Methyl nitrite, $CH_3 \cdot O \cdot NO$
Explodes on sudden heating.

b.p.

17° Ethyl nitrite, $C_2H_5{\cdot}O{\cdot}NO$, d_4^{15} 0·900.

49° *n*-Propyl nitrite, $C_3H_7{\cdot}O{\cdot}NO$, d 0·935.

65° Methyl nitrate, $CH_3{\cdot}O{\cdot}NO_2$, d_4^{15} 1·217.

87° Ethyl nitrate, $C_2H_5{\cdot}O{\cdot}NO_2$, d_4^{15} 1·116.

99° *iso*Amyl nitrite, $(CH_3)_2CH{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}NO$, d_4^{15} 0·880.

110° *n*-Propyl nitrate, $C_3H_7{\cdot}O{\cdot}NO_2$, d_4^{15} 1·063.

188° Dimethyl sulphate, $CH_3O{\cdot}SO_2{\cdot}OCH_3$, d_{15}^{15} 1·333.
Poisonous.
Tribromophenol ⟶ methyl ether, needles, m.p. 87°.

208° Diethyl sulphate, $C_2H_5O{\cdot}SO_2{\cdot}OC_2H_5$.
Tribromophenol ⟶ ethyl ether, needles, m.p. 72°.

Acid Chlorides

(General tests, see p. 68)

Liquids

51° Acetyl chloride, $CH_3{\cdot}CO{\cdot}Cl$.
Aniline ⟶ acetanilide, plates (water), m.p. 114°.

64° Oxalyl chloride, $Cl{\cdot}CO{\cdot}CO{\cdot}Cl$.
Aniline ⟶ oxanilide, m.p. 257°.

80° Propionyl chloride, $C_3H_7{\cdot}CO{\cdot}Cl$.
Aniline ⟶ propionanilide, plates, m.p. 103°.

81° Acetyl bromide, $CH_3{\cdot}CO{\cdot}Br$.
Aniline ⟶ acetanilide, plates (water), m.p. 114°.

108–111° Chloracetyl chloride, $CH_2Cl{\cdot}CO{\cdot}Cl$.
Aniline ⟶ chloracetanilide, needles (water), m.p. 134°.

197° Benzoyl chloride, $C_6H_5{\cdot}CO{\cdot}Cl$.
Aniline ⟶ benzanilide, hexagonal prisms, m.p. 163°.

218° Benzoyl bromide, $C_6H_5{\cdot}CO{\cdot}Br$.
Aniline ⟶ benzanilide, hexagonal prisms, m.p. 163°.

210° Phenylacetyl chloride, $C_6H_5{\cdot}CH_2{\cdot}CO{\cdot}Cl$.
Aniline ⟶ phenylacetanilide, plates (aq. alcohol), m.p. 117°.

Solids

m.p.

75° *p*-Nitrobenzoyl chloride, $NO_2 \cdot C_6H_4 \cdot CO \cdot Cl$.
Ammonia ⟶ *p*-nitrobenzamide, cubic prisms, m.p. 201°.

69° 3 : 5-Dinitrobenzoyl chloride.
Amide : plates, m.p. 183°.

Amides, Imides, and Ureas

(General tests, see p. 68)

Liquid

b.p.

195° Formamide, $H \cdot CO \cdot NH_2$.
Deliquescent.
H_2SO_4 (warming) ⟶ CO.
Formyl phenylhydrazide : plates (water), m.p 145°.

Solids

m.p.

49° Ethyl carbamate, $NH_2 \cdot CO \cdot OC_2H_5$.
Weak iodoform test.
On gentle heating gives off ethyl alcohol which burns with pale blue flame.

79° Propionamide, $CH_3 \cdot CH_2 \cdot CO \cdot NH_2$.

82° Acetamide, $CH_3 \cdot CO \cdot NH_2$.
Deliquescent. Mouse-like odour when impure.
Aceto-*p*-toluidide (2 hrs. heating with *p*-toluidine), prisms, m.p. 147°.

96° Semicarbazide, $NH_2 \cdot CO \cdot NH \cdot NH_2$.
Generally obtained in the form of its salts.
Reduces Fehling's soln. and Tollen's soln.
Forms crystalline semicarbazones with aldehydes and ketones.

97° *m*-Toluamide, $CH_3 \cdot C_6H_4 \cdot CO \cdot NH_2$.
Hydrolysis (50% H_2SO_4) ⟶ *m*-toluic acid, prisms (aq. alcohol), m.p. 112°.

102° Methylurea, $CH_3 \cdot NH \cdot CO \cdot NH_2$.
Picrate : elongated yellow prisms, m.p. 127° (d).

m.p.

125° Succinimide, $\begin{matrix} CH_2{\cdot}CO \\ CH_2{\cdot}CO \end{matrix}{>}NH$

130° Benzamide, $C_6H_5{\cdot}CO{\cdot}NH_2$.
Hydrolysis (50% H_2SO_4) ⟶ benzoic acid, plates (water), m.p. 122°.

132° Urea, $NH_2{\cdot}CO{\cdot}NH_2$.
Picrate: elongated yellow needles, m.p. 148°.
Oxalate: conc. solns. of urea and oxalic acid on mixing give a ppt. of urea oxalate: colourless hexagonal prisms.
After being heated gives biuret test.

134° *m*-Chlorobenzamide, $Cl{\cdot}C_6H_4{\cdot}CO{\cdot}NH_2$.
Hydrolysis (50% H_2SO_4) ⟶ *m*-chlorobenzoic acid, prisms, m.p. 158°.

139° Salicylamide, $HO{\cdot}C_6H_4{\cdot}CO{\cdot}NH_2$ (1 : 2).
$FeCl_3$: violet (water or alcohol).
Hydrolysis (50% H_2SO_4) ⟶ salicyclic acid, needles (water) m.p. 159°.

142° *o*-Toluamide, $CH_3{\cdot}C_6H_4{\cdot}CO{\cdot}NH_2$.
Hydrolysis (50% H_2SO_4) ⟶ *o*-toluic acid, needles (aq. alcohol), m.p. 107°.

142° *o*-Chlorobenzamide, $Cl{\cdot}C_6H_4{\cdot}CO{\cdot}NH_2$.
Hydrolysis (50% H_2SO_4) ⟶ *o*-chlorobenzoic acid, prisms (aq. alcohol), m.p. 142°. (Mixed m.p.; cf. m.p. of amide.)

147° Phenylurea, $C_6H_5{\cdot}NH{\cdot}CO{\cdot}NH_2$.
See p. 184.

154° Phenylacetamide, $C_6H_5{\cdot}CH_2{\cdot}CO{\cdot}NH_2$.
Hydrolysis (50% H_2SO_4) ⟶ phenylacetic acid, plates (water), m.p. 78°.

157° *o*-Bromobenzamide, $Br{\cdot}C_6H_4{\cdot}CO{\cdot}NH_2$.
Hydrolysis (50% H_2SO_4) ⟶ *o*-bromobenzoic acid, needles (aq. alcohol), m.p. 150°.

155° *m*-Bromobenzamide, $Br{\cdot}C_6H_4{\cdot}CO{\cdot}NH_2$.
Hydrolysis (50% H_2SO_4) ⟶ *m*-bromobenzoic acid, needles (aq. alcohol), m.p. 155° (mixed m.p.; cf. m.p. of amide).

m.p.

160° *p*-Toluamide, $CH_3 \cdot C_6H_4 \cdot CO \cdot NH_2$.
Hydrolysis (50% H_2SO_4) $\longrightarrow$ *p*-toluic acid, prisms (aq. alcohol), m.p. 178°.

170°(d) Alloxan, $CO<\begin{smallmatrix}NH \cdot CO \\ NH \cdot CO\end{smallmatrix}>CO$
Crystallises with 4 molecules of water.
Heating $\longrightarrow CO_2 + CO + NH_3$.

170° Malonamide, $NH_2 \cdot CO \cdot CH_2 \cdot CO \cdot NH_2$.

176° *o*-Nitrobenzamide, $NO_2 \cdot C_6H_4 \cdot CO \cdot NH_2$.
Hydrolysis (50% H_2SO_4) $\longrightarrow$ *o*-nitrobenzoic acid, needles (water), m.p. 147°.

179° *p*-Chlorobenzamide, $Cl \cdot C_6H_4 \cdot CO \cdot NH_2$.
Hydrolysis (50% H_2SO_4) $\longrightarrow$ *p*-chlorobenzoic acid, prisms, m.p. 243°.

189° *p*-Bromobenzamide, $Br \cdot C_6H_4 \cdot CO \cdot NH_2$.
Hydrolysis (50% H_2SO_4) $\longrightarrow$ *p*-bromobenzoic acid, plates (water), m.p. 254°.

190° (d) Biuret, $NH_2 \cdot CO \cdot NH \cdot CO \cdot NH_2$.
Biuret reaction: copper sulphate and NaOH give a violet coloration.

201° *p*-Nitrobenzamide, $NO_2 \cdot C_6H_4 \cdot CO \cdot NH_2$.
Hydrolysis (50% H_2SO_4) $\longrightarrow$ *p*-nitrobenzoic acid, plates (aq. alcohol), m.p. 242°.

202° α-Naphthoic amide, $C_{10}H_7 \cdot CO \cdot NH_2$.
Hydrolysis (50% H_2SO_4) $\longrightarrow$ small yield of α-naphthoic acid after 3 hrs.' hydrolysis. Hydrolysis (50% H_2SO_4 and acetic acid) $\longrightarrow$ α-naphthoic acid, plates, m.p. 162°.

233° Phthalimide, $C_6H_4<\begin{smallmatrix}CO \\ CO\end{smallmatrix}>NH$
Sublimes.
Hydrolysis (50% H_2SO_4) $\longrightarrow$ phthalic acid, cubic prisms (aq. alcohol), m.p. 195° (approx.).
Ammonia $\longrightarrow$ phthalamide: 0·05 g. phthalimide is heated with conc. ammonia for 30 sec. and the soln. allowed to stand for 30 mins. The white ppt. of phthalamide is washed with a little alcohol: m.p. 220° (d).

m.p.

220° Phthalamide, $C_6H_4(CO{\cdot}NH_2)_2$ 1 : 2.
Hydrolysis (50% H_2SO_4) ⟶ phthalic acid, cubic prisms (aq. alcohol), m.p. 195° (approx.).

245° Barbituric acid, $CO<\begin{matrix}NH{\cdot}CO\\NH{\cdot}CO\end{matrix}>CH_2$
Boiling with NaOH gives ammonia and sodium malonate.

250° Succindiamide, $\begin{matrix}CH_2{\cdot}CO{\cdot}NH_2\\|\\CH_2{\cdot}CO{\cdot}NH_2\end{matrix}$
Heating ⟶ succinimide, m.p. 125°.

300° Oxamide, $\begin{matrix}CO{\cdot}NH_2\\|\\CO{\cdot}NH_2\end{matrix}$
Red colour with $CuSO_4$ and NaOH.
H_2SO_4 (heat) ⟶ $CO_2 + CO$.

Nitriles

(General tests, see p. 69)

Liquids

b.p.

82° Acetonitrile, $CH_3{\cdot}CN$, d 0·7822.
Agreeable bitter-almond odour. Burns with peach-coloured flame.

97° Propionitrile, $C_2H_5{\cdot}CN$, d 0·7822.
Agreeable bitter-almond odour.

118° *n*-Butyronitrile, $C_3H_7{\cdot}CN$, d 0·7914.
Agreeable bitter-almond odour.

141° *n*-Valeronitrile, $C_4H_9{\cdot}CN$, d 0·7992.
Agreeable bitter-almond odour.

170° Mandelonitrile, $C_6H_5{\cdot}CHOH{\cdot}CN$.
Hydrolysis (50% H_2SO_4) ⟶ mandelic acid, which is obtained by extraction with ether: m.p. 120°.

191° Benzonitrile, $C_6H_5{\cdot}CN$.
Agreeable bitter-almond odour.
Hydrolysis (50% H_2SO_4) ⟶ benzoic acid, plates (water), m.p. 122°.

205° *o*-Tolunitrile, $CH_3{\cdot}C_6H_4{\cdot}CN$.
Hydrolysis (50% H_2SO_4) ⟶ *o*-toluic acid, needles (aq. alcohol), m.p. 107°.

b.p.

212° *m*-Tolunitrile, $CH_3 \cdot C_6H_4 \cdot CN$.
Hydrolysis (50% H_2SO_4) ⟶ *m*-toluic acid, prisms (aq. alcohol), m.p. 112°.

212° Benzyl cyanide, $C_6H_5 \cdot CH_2 \cdot CN$.
Hydrolysis (50% H_2SO_4) ⟶ phenylacetic acid, plates (water), m.p. 78°.

Solids

m.p.

37° α-Naphthonitrile, $C_{10}H_7 \cdot CN$.
Hydrolysis (50% H_2SO_4—2 hrs.) ⟶ α-naphthoamide, prisms (aq. alcohol), m.p. 202°.

38° *p*-Tolunitrile, $CH_3 \cdot C_6H_4 \cdot CN$.
Hydrolysis (saturated aq. soln. of NaOH—$\frac{3}{4}$ hr.) ⟶ *p*-toluamide, m.p. 160°.
Hydrolysis (50% H_2SO_4) ⟶ *p*-toluic acid, prisms (aq. alcohol), m.p. 178°.

66° β-Naphthonitrile, $C_{10}H_7 \cdot CN$.
Hydrolysis (50% H_2SO_4—2 hrs.) ⟶ β-naphthoic acid, prisms (aq. alcohol), m.p. 186°.

69° Cyanacetic acid, $CN \cdot CH_2 \cdot COOH$.
Hydrolysis (NaOH) ⟶ sodium malonate, identified as *p*-nitrobenzyl ester, m.p. 85°.

148° *p*-Nitrobenzonitrile, $NO_2 \cdot C_6H_4 \cdot CN$.
Hydrolysis (50% H_2SO_4) ⟶ *p*-nitrobenzoic acid, plates (aq. alcohol), m.p. 242°.

Amines

Primary and Secondary

(General tests, see pp. 69–73. Colour tests, see p. 46)

Liquids

b.p.

Gas Methylamine, $CH_3 \cdot NH_2$.
Characteristic odour. Usually obtained in aqueous or alcoholic solution.
Phenylthiourea : plates (aq. alcohol), m.p. 113°.
Picrate : yellow prisms, m.p. 206°.
2 : 4-Dinitro-*N*-methylaniline : yellow plates, m.p. 176°.

b.p.

7° Dimethylamine, $(CH_3)_2NH$.
Characteristic odour. Usually obtained in aqueous or alcoholic solution.
Phenylthiourea: plates (aq. alcohol), m.p. 135°.
Picrate: yellow plates, m.p. 158°.

17° Ethylamine, $C_2H_5 \cdot NH_2$.
Characteristic odour. Usually obtained in alcoholic or aqueous solution.
Phenylthiourea: plates, m.p. 95°.
Picrate: yellow prisms, m.p. 166°.
2 : 4-Dinitro-*N*-ethylaniline: yellow plates, m.p. 114°.

32° *iso*Propylamine, $(CH_3)_2CH \cdot NH_2$.
Characteristic odour.
Phenylthiourea: plates, m.p. 101°.

49° *n*-Propylamine, $C_3H_7 \cdot NH_2$.
Characteristic odour.
Phenylthiourea: cubic prisms, m.p. 63°. If an oil is obtained it is allowed to stand until it solidifies.
Dipropyloxamide: plates, m.p. 165°.

55° Diethylamine, $(C_2H_5)_2NH$.
Characteristic odour.
4-Diphenylthiourea: m.p. 114°.
β-Naphthylthiourea: needles, m.p. 90°.
Picrate: yellow, m.p. 155°.

56° Allylamine, $CH_2{:}CH \cdot CH_2 \cdot NH_2$.
Picrate: m.p. 140°.
Diallyloxamide: plates, m.p. 154°.

63° *sec.*-*n*-Butylamine, $C_2H_5 \cdot CH(NH_2) \cdot CH_3$
Phenylthiourea: m.p. 101°.
Picrate: yellow plates, m.p. 139°.

68° *iso*Butylamine, $(CH_3)_2CH \cdot CH_2 \cdot NH_2$.
Di*iso*butyloxamide: plates, m.p. 167°.

78° *n*-Butylamine, $C_4H_9 \cdot NH_2$.
Characterstic odour.
Phenylthiourea: square plates, m.p. 65°.

b.p.

Picrate: yellow needles, m.p. 151°.
Dibutyloxamide: plates, m.p. 153°.

95° *iso*Amylamine, $(CH_3)_2CH \cdot CH_2 \cdot CH_2 \cdot NH_2$.
Phenylthiourea: m.p. 102°.
β-Naphthylthiourea: prisms, m.p. 116°.
4-Diphenylthiourea: needles, m.p. 130°.

104° *n*-Amylamine, $C_5H_{11} \cdot NH_2$.
Phenylthiourea: m.p. 69°.
β-Naphthylthiourea: prisms, m.p. 114°.
4-Diphenylthiourea: needles, m.p. 147°.

116° Ethylenediamine, $NH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2$.
Crystallises with 1 mol. of water, m.p. 10°.
β-Naphthylthiourea: needles, m.p. 223°.
Dibenzenesulphonyl derivative: elongated prisms, m.p. 168°.
Heated with benzil in alcoholic soln. for 30 mins. gives yellow prisms of 2 : 3-diphenyl-5 : 6-dihydropyrazine, m.p. 160°.
Picrate: yellow plates, m.p. 233°.

184° Aniline, $C_6H_5 \cdot NH_2$, d 1·0218.
Characteristic odour, different from that of the aliphatic amines. Colourless liquid which rapidly turns brown on exposure to air.
Runge's test: dil. soln. of bleaching-powder gives violet coloration.
Acetyl derivative: plates, m.p. 114°.
Benzoyl derivative: plates, m.p. 163°.
p-Toluenesulphonyl derivative: prisms, m.p. 103°.
HCl salt: m.p. 198°.
Phenylthiourea: plates, m.p. 154°.

185° Benzylamine, $C_6H_5 \cdot CH_2 \cdot NH_2$.
Forms solid carbonate on exposure to the atmosphere.
Dibenzyloxamide: elongated prisms (acetic acid), m.p. 222°.
Benzoyl derivative: m.p. 105°.
Picrate: yellow prisms, m.p. 194–6° (d).

b.p.

196° *N*-Methylaniline, $C_6H_5{\cdot}NH{\cdot}CH_3$.

A green colour is obtained by dissolving a drop of the compound in conc. HCl, adding 3 drops $FeCl_3$, and boiling.

Acetyl derivative: m.p. 102°.

p-Toluenesulphonyl derivative: m.p. 94°.

HCl salt: m.p. 121°.

Phenylthiourea: m.p. 87°.

Picrate: prepared in ether soln.: needles (ether), m.p. 145° (d).

200° *o*-Toluidine, $CH_3{\cdot}C_6H_4{\cdot}NH_2$.

Acetyl derivative: plates, m.p. 112° (mixed m.p. necessary: cf. m.p. of acetanilide).

Benzoyl derivative: prisms (acetic acid), m.p. 142°.

Benzenesulphonyl derivative: plates, m.p. 124°.

HCl salt: needles, m.p. 215°.

Phenylthiourea: m.p. 136°.

Picrate: yellow prisms, m.p. about 213° (d).

Bromination (acetic acid) ⟶ hydrobromide of 3 : 5-dibromo-2-aminotoluene: square plates (acetic acid), high m.p.

203° *m*-Toluidine, $CH_3{\cdot}C_6H_4{\cdot}NH_2$.

Benzoyl derivative: plates, m.p. 125°.

p-Toluenesulphonyl derivative: m.p. 114°.

HCl salt: needles, m.p. 236°.

Phenylthiourea: hexagonal prisms, m.p. 94°.

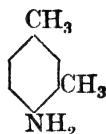
Picrate: yellow plates: chars at 200°.

Bromination (acetic acid) ⟶ 2 : 4 : 6-tribromo-3-aminotoluene, needles (acetic acid), m.p. 97°.

206° *N*-Ethylaniline, $C_6H_5{\cdot}NH{\cdot}C_2H_5$.

Colour test as for *N*-methylaniline.

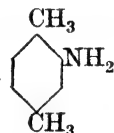
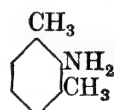
p-Toluenesulphonyl derivative: elongated prisms, m.p. 87°.

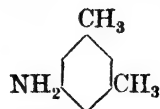
HCl salt: m.p. 176°.

Phenylthiourea: m.p. 89°.

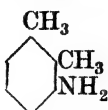
Picrate (ether soln.): yellow prisms, m.p. 138° (d).

b.p.

212° 4-Amino-1 : 3-dimethylbenzene (ring: CH_3 at 1, CH_3 at 3, NH_2 at 4)

Acetyl derivative : prisms, m.p. 128°.
Benzoyl derivative : prisms, m.p. 192°.
Benzenesulphonyl derivative : prisms, m.p. 128°.
HCl salt : m.p. 235° (d).
Phenylthiourea : plates, m.p. 152°.
Picrate : yellow needles : chars at 205°.

215° 2-Amino-1 : 4-dimethylbenzene, (ring: CH_3 at 1, NH_2 at 2, CH_3 at 4)

Acetyl derivative : needles, m.p. 139°.
Benzoyl derivative : prisms, m.p. 150°.
Benzenesulphonyl derivative : prisms, m p 138°.
Phenylthiourea : plates, m.p. 148°.
Picrate : yellow needles, decompose at 171°.

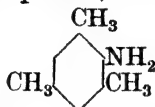
216° 2-Amino-1 : 3-dimethylbenzene, (ring: CH_3 at 1, NH_2 at 2, CH_3 at 3)

Acetyl derivative : needles, m.p. 176°.
Benzoyl derivative : elongated prisms, m.p. 170°.
Phenylthiourea : needles, m.p. 204°.
Picrate : yellow cubic prisms, decompose about 180°.

220° 5-Amino-1 : 3-dimethylbenzene, (ring: CH_3 at 1, CH_3 at 3, NH_2 at 5)

Acetyl derivative : elongated prisms, m.p. 144°.
Benzoyl derivative : elongated prisms, m.p. 136°.
Phenylthiourea : plates, m.p. 153°.
Picrate : yellow needles, decompose at 200°.

b.p.

221° 3-Amino-1 : 2-dimethylbenzene, (ring with CH_3, CH_3, NH_2)

Acetyl derivative: needles, m.p. 136°.
Benzoyl derivative: prisms, m.p. 189°.
Picrate: yellow prisms; decompose at 221°.

229° Mesidine, (ring with CH_3, NH_2, CH_3, CH_3)

Acetyl derivative: m.p. 216°.
Benzoyl derivative: prisms, m.p. 206°.
Phenylthiourea: m.p. 193°.

Solids

m.p.

37° *N*-Benzylaniline, $C_6H_5 \cdot NH \cdot CH_2 \cdot C_6H_5$.
Benzoyl derivative: sometimes obtained as an oil which solidifies over-night: prisms, m.p. 107°.
Benzenesulphonyl derivative: elongated prisms, m.p. 119°.
HCl salt: m.p. 214–216°.
s.-Trinitrobenzene derivative: red plates, m.p. 95°.

30° 3-Aminodiphenyl, $C_6H_5 \cdot C_6H_4 \cdot NH_2$.
Acetyl derivative: cubic prisms (aq. alcohol), m.p. 148°.
Benzoyl derivative: needles, m.p. 135°.

44° *p*-Toluidine, $CH_3 \cdot C_6H_4 \cdot NH_2$, b.p. 201°.
Acetyl derivative: elongated prisms, m.p. 153°.
Benzoyl derivative: prisms, m.p. 158°.
Phenylthiourea: m.p. 141°.
p-Toluenesulphonyl derivative: prisms, m.p. 108°.
HCl salt: m.p. 236° (d).
Picrate: yellow needles: decomposes at 182°.
Bromination (acetic acid) ⟶ 3 : 5-dibromo-4-aminotoluene, needles (acetic acid), m.p. 73°.

49° 2-Aminodiphenyl, $C_6H_5 \cdot C_6H_4 \cdot NH_2$.
Acetyl derivative: prisms (aq. alcohol), m.p. 119°.
Benzoyl derivative: needles, m.p. 102°.

m.p.

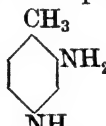
50° α-Naphthylamine, $C_{10}H_7{\cdot}NH_2$.

Acetyl derivative : needles, m.p. 160°.
Benzoyl derivative : needles, m.p. 169°.
Phenylthiourea : hexagonal plates, m.p. 165°.
p-Toluenesulphonyl derivative : prisms, m.p. 157°.
HCl salt : m.p. 260° (d).
Picrate : yellow plates : decomposes at 163°.

53° 4-Aminodiphenyl, $C_6H_5{\cdot}C_6H_4{\cdot}NH_2$.

Acetyl derivative : needles, m.p. 171°.
Benzoyl derivative : rhombic plates (acetic acid), m.p. 235°.
Phenylthiourea : prisms, m.p. 211°.

54° Diphenylamine, $C_6H_5{\cdot}NH{\cdot}C_6H_5$.

Weak base. Salts hydrolysed.
Benzoyl derivative : prisms, m.p. 180°.
Bromination (acetic acid) ⟶ hexabromo-compound, needles (benzene), m.p. 218°.

63° *m*-Phenylenediamine, $NH_2{\cdot}C_6H_4{\cdot}NH_2$.

Quickly darkens on exposure to air. It is frequently difficult to prepare derivatives from the impure compound.
Diacetyl derivative : m.p. 191°.
Dibenzoyl derivative : m.p. 240°.

99° 2 : 4-Diaminotoluene, (benzene ring with CH_3 at 1, NH_2 at 2, NH_2 at 4)

CH_3
NH_2
NH_2

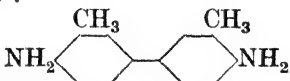
Darkens rapidly on exposure to air.
Diacetyl derivative : prisms (aq. alcohol), m.p. 220°.
Picrate : brown prisms, m.p. about 170° (d).

102° *o*-Phenylenediamine, $NH_2{\cdot}C_6H_4{\cdot}NH_2$.

The diamine in HCl soln. gives a red colour with $FeCl_3$.
Diacetyl derivative : the diamine (0·2 g.) is shaken with water (1 c.c.) and 12 drops of acetic anhydride until a clear soln. is obtained. Cubic prisms of the diacetate soon separate : m.p. 185°.

m.p.

Picrate: orange prisms; chars at 195°.
Benzil ⟶ quinoxaline: needles, m.p. 124°.

112° β-Naphthylamine, $C_{10}H_7 \cdot NH_2$.
Volatile in steam. Sublimes.
Acetyl derivative: plates, m.p. 136°.
Benzoyl derivative: elongated prisms, m.p. 162°.
Phenylthiourea: plates, m.p. 129°.
p-Toluenesulphonyl derivative: prisms, m.p. 133°.
HCl salt: m.p. 286° (d).
Picrate: yellow needles: chars at 195°.

127° Benzidine, $NH_2 \cdot C_6H_4 \cdot C_6H_4 \cdot NH_2$.
Dibenzenesulphonyl derivative: purified by washing with boiling alcohol: m.p. 232°.
Di-*p*-toluenesulphonyl derivative: purified as above: m.p. 243°.

129° *o*-Tolidine, NH_2–$C_6H_3(CH_3)$–$C_6H_3(CH_3)$–NH_2
Dibenzal derivative: needles (ligroin), m.p. 148°.
Dibenzoyl derivative: m.p. 265°.

140° *p*-Phenylenediamine, $NH_2 \cdot C_6H_4 \cdot NH_2$.
$FeCl_3$: dark green colour.
2:4-Dinitrophenyl derivative: red plates, m.p. 190°.
Picrate: yellow hexagonal plates, m.p. 202°.

Amines

Tertiary

(General tests, see pp. 69–73)

Liquids

b.p.

Gas Trimethylamine, $(CH_3)_3N$.
Usually obtained in aq. soln.
Picrate: yellow prisms, m.p. 225°.
CH_3I ⟶ tetramethylammonium iodide, decomp. at 230°.

89° Triethylamine, $(C_2H_5)_3N$.
Picrate: yellow prisms, m.p. 173°.

b.p.

185° *N*,*N*-Dimethyl-*o*-toluidine, $(CH_3)_2N\cdot C_6H_4\cdot CH_3$.
Picrate : yellow prisms, m.p. 122°.
HCl salt : hygroscopic.

194° *N*,*N*-Dimethylaniline, $C_6H_5\cdot N(CH_3)_2$, d 0·9563.
M.p. 2–3°.
Picrate : yellow hexagonal prisms, m.p. 163°.
Methiodide : white plates : sublimes at 225°.
HCl salt : m.p. 85–95° : hygroscopic.

210° *N*,*N*-Dimethyl-*p*-toluidine, $CH_3\cdot C_6H_4\cdot N(CH_3)_2$.
Picrate : yellow prisms, m.p. 129°.
Methiodide : plates, m.p. 220°.
HCl salt : m.p. 143°.

212° *N*,*N*-Dimethyl-*m*-toluidine, $CH_3\cdot C_6H_4\cdot N(CH_3)_2$.
Picrate : yellow cubic prisms, m.p. 132°.
Methiodide : plates, m.p. 185° (d).

216° *N*,*N*-Diethylaniline, $C_6H_5\cdot N(C_2H_5)_2$.
Picrate : yellow prisms, m.p. 142°.
Methiodide : m.p. 102°.

Solids

m.p.

91° Tribenzylamine, $(C_6H_5\cdot CH_2)_3N$.
Very weak base.
Picrate : yellow prisms, m.p. 190°.

127° Triphenylamine, $(C_6H_5)_3N$.
Very weak base. Does not form salts with acids.
Nitration (fuming HNO_3 and acetic acid) ⟶ trinitro-derivative, m.p. 280°, after washing with boiling alcohol.

Halogen Substituted Amines

Liquids

b.p.

209° *o*-Chloraniline, $NH_2\cdot C_6H_4\cdot Cl$.
Picrate : yellow prisms, m.p. 139° (d).
Acetyl derivative : elongated prisms (aq. alcohol), m.p. 87°.

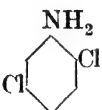
b.p.

Benzoyl derivative : prisms, m.p. 99°.
Phenylthiourea : plates, m.p. 156°.

230° *m*-Chloraniline, $Cl{\cdot}C_6H_4{\cdot}NH_2$.
Acetyl derivative : needles, m.p. 72°.
Benzoyl derivative : needles, m.p. 121°.
Phenylthiourea : m.p. 116°.

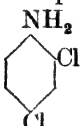
Solids

m.p.

18° *m*-Bromaniline, $Br{\cdot}C_6H_4{\cdot}NH_2$, b.p. 251°.
Acetyl derivative : needles, m.p. 88°.
Benzoyl derivative : prisms, m.p. 137°.
Picrate : yellow prisms, decompose at 187°.

32° *o*-Bromaniline, $NH_2{\cdot}C_6H_4{\cdot}Br$.
Acetyl derivative : m.p. 99°.
Benzoyl derivative : prisms, m.p. 116°.
Picrate (prepared in ether soln.) : needles, m.p. about 165° (d).

50° 2 : 5-Dichloraniline, NH_2, Cl, Cl

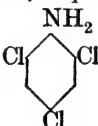
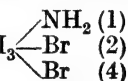
Acetyl derivative : elongated prisms, m.p. 132°.
Benzoyl derivative : needles, m.p. 120°.

59° *o*-Iodoaniline, $NH_2{\cdot}C_6H_4{\cdot}I$.
Acetyl derivative : m.p. 109°.
Benzoyl derivative : prisms, m.p. 139°.

62° *p*-Iodoaniline, $I{\cdot}C_6H_4{\cdot}NH_2$.
Acetyl derivative : m.p. 183°.
Benzoyl derivative : m.p. 222°.

63° 2 : 4-Dichloraniline,

Acetyl derivative : octahedra, m.p. 147°.
Benzoyl derivative : prisms, m.p. 117°.
Benzenesulphonyl derivative : needles, m.p. 128°.

m.p.

66° *p*-Bromaniline, $Br{\cdot}C_6H_4{\cdot}NH_2$.
Acetyl derivative: prisms, m.p. 167°.
Benzoyl derivative: plates (acetic acid), m.p. 204°.
Picrate, prepared in ether soln.: prisms, decompose at 180°.

70° *p*-Chloraniline, $Cl{\cdot}C_6H_4{\cdot}NH_2$.
Acetyl derivative: plates, m.p. 179°.
Benzoyl derivative: plates, m.p. 193°.
Benzenesulphonyl derivative: hexagonal plates, m.p. 121°.
Picrate: yellow prisms, m.p. 187° (d).

77° 2 : 4 : 6-Trichloraniline,

Monoacetyl derivative: the amine is dissolved in acetic anhydride and a drop of conc. H_2SO_4 is added The soln. is shaken for 2 mins. and poured into water. The ppt. is crystallised from alcohol: prisms, m.p. 208°.

79° 2 : 4-Dibromaniline, $C_6H_3 \begin{cases} NH_2 & (1) \\ Br & (2) \\ Br & (4) \end{cases}$

Acetyl derivative: m.p. 146°.
Benzoyl derivative: m.p. 134°.

119° 2 : 4 : 6-Tribromaniline,

Very weak base: insoluble in conc. HCl, prisms.
Monoacetyl derivative: (see trichloraniline), m.p. 232°.

Nitro-Amines

Solids

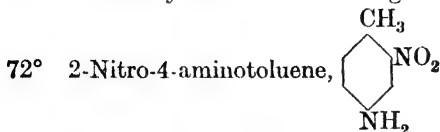
71° *o*-Nitraniline, $NH_2{\cdot}C_6H_4{\cdot}NO_2$.
Yellow.
Volatile in steam.

m.p.

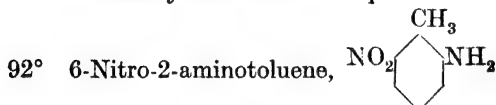
Acetyl derivative : m.p. 92°.
Benzoyl derivative : elongated prisms, m.p. 94°.

CH_3

72° 2-Nitro-4-aminotoluene, NO_2

NH_2

Acetyl derivative : m.p. 93°.
Benzoyl derivative : m.p. 172°

CH_3

92° 6-Nitro-2-aminotoluene, NO_2 NH_2

Acetyl derivative : m.p. 157°.
Benzoyl derivative : m.p. 167°

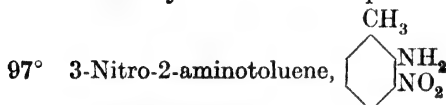
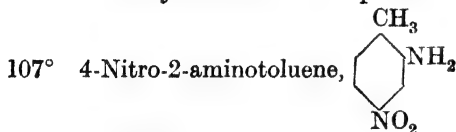
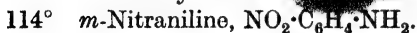
CH_3

97° 3-Nitro-2-aminotoluene, NH_2 NO_2

Acetyl derivative : m.p. 158°.

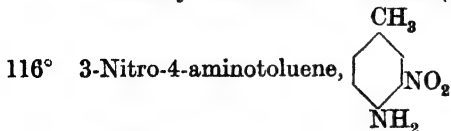
CH_3

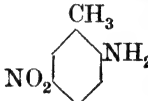
107° 4-Nitro-2-aminotoluene, NH_2

NO_2

Yellow.
Acetyl derivative : needles (aq. alcohol), m.p. 152°.
Benzoyl derivati[illegible]dles, m.p. 186°.

114° *m*-Nitraniline, $NO_2 \cdot C_6H_4 \cdot NH_2$.
Yellow. Volatile in steam.
Acetyl derivative : needles, m.p. 155°.
Benzoyl derivative : needles (acetic acid), m.p. 158°.

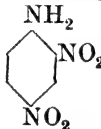
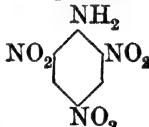
CH_3

116° 3-Nitro-4-aminotoluene, NO_2

NH_2

Red.
Acetyl derivative : yellow needles, m.p. 96°.
Benzoyl derivative : yellow prisms, m.p. 143°

m.p.

126° 1-Nitro-β-naphthylamine, $NH_2 \cdot C_{10}H_6 \cdot NO_2$.
Dark yellow.
Benzoyl derivative: prisms, m.p. 224°.
Acetyl derivative: pale yellow needles, m.p. 124°. Mixed m.p. with the nitro-amine necessary.
s.-Trinitrobenzene derivative: orange needles, m.p. 115°.

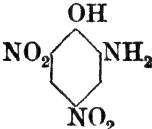
130° 5-Nitro-2-aminotoluene, (CH_3, NH_2, NO_2 ring)
Yellow.
Acetyl derivative: needles, m.p. 202°.
Benzoyl derivative: needles (acetic acid), m.p. 174°.

144° 2-Nitro-α-naphthylamine, $NH_2 \cdot C_{10}H_6 \cdot NO_2$.
Acetyl derivative: m.p. 199°.

147° *p*-Nitraniline, $NO_2 \cdot C_6H_4 \cdot NH_2$.
Yellow. Not volatile in steam.
Acetyl derivative: needles, m.p. 215°.
Benzoyl derivative: hexagonal plates, m.p. 199°.

179° 2 : 4-Dinitraniline, (NH_2, NO_2, NO_2 ring)
Yellow.
Acetyl derivative: prisms, m.p. 120°.

190° Picramide, (NH_2, NO_2, NO_2, NO_2 ring)
Yellow.
Molecular compound with naphthalene (prepared in acetic acid), orange prisms, m.p. 168°.

196° 4-Nitro-α-naphthylamine, $NH_2 \cdot C_{10}H_6 \cdot NO_2$.
Yellow.
Acetyl derivative: m.p. 190°.
Benzoyl derivative: purified by boiling with alcohol: m.p. 224°.

Hydroxy- and Alkoxy-Amines

Liquids

b.p.

225° *o*-Anisidine, $NH_2 \cdot C_6H_4 \cdot OCH_3$.
Acetyl derivative: elongated prisms, m.p. 85°.
Benzoyl derivative: cubic prisms, m.p. 64°.
Phenylthiourea: plates or prisms, m.p. 136°.
p-Toluenesulphonyl derivative: needles or plates, m.p. 127°.
Picrate: yellow needles, m.p. 200° (d).

229° *o*-Phenetidine, $NH_2 \cdot C_6H_4 \cdot OC_2H_5$.
Acetyl derivative: m.p. 79°.
Thiourea: m.p. 137°.

254° *p*-Phenetidine, $C_2H_5O \cdot C_6H_4 \cdot NH_2$.
Red colour with HCl and $FeCl_3$.
Acetyl derivative: prisms, m.p. 135°.
Benzoyl derivative: plates, m.p. 173°.
Phenylthiourea: plates, m.p. 136°. Mixed m.p., cf. m.p. of phenylthiourea of *o*-anisidine.

Solids

m.p.

57° *p*-Anisidine, $CH_3O \cdot C_6H_4 \cdot NH_2$.
Acetyl derivative: plates, m.p. 130°.
Benzoyl derivative: hexagonal plates, m.p. 157°.
Phenylthiourea: plates, m.p. 157°.
Benzenesulphonyl derivative: m.p. 95°, needles (aq. alcohol).
Picrate: elongated prisms, m.p. 170° (d).

81° Phenylhydroxylamine, $C_6H_5 \cdot NHOH$.
Dangerous to the skin.
Reduces Fehling's and Tollen's solution immediately in the cold.

122° *m*-Aminophenol, $NH_2 \cdot C_6H_4 \cdot OH$.
Dibenzoyl derivative: cubic prisms, m.p. 153°.
Phenylthiourea: plates, m.p. 156°

m.p.

168° Picramic acid, (structure: benzene ring with OH at top, NO_2 and NH_2 on either side, NO_2 at bottom)

Brownish-red.

Acetyl derivative: prisms, m.p. 201°.

174° *o*-Aminophenol, $HO{\cdot}C_6H_4{\cdot}NH_2$.

Sublimes.

$FeCl_3$: brown colour (alcohol).

Acetic anhydride ⟶ benzoxazole derivative, square plates (acetic anhydride), m.p. 205°.

Dibenzoyl derivative: needles (acetic acid), m.p. 182°.

Phenylthiourea: plates, m.p. 146°.

184° (d) *p*-Aminophenol, $NH_2{\cdot}C_6H_4{\cdot}OH$.

Sublimes.

$FeCl_3$: purple (water).

Acetyl derivative: m.p. 168°.

Dibenzoyl derivative: prisms, m.p. 234°.

Phenylthiourea: hexagonal plates, m.p. 150°.

Anilides and Toluidides

(General tests, see p. 74. Colour tests, see p. 42)

Derivatives are made in most cases by hydrolysing the anilides or toluidides with 50% sulphuric acid (p. 91) and isolating the acid or amine.

Solids

50° Formanilide, $C_6H_5{\cdot}NH{\cdot}CHO$.

It is readily hydrolysed in aq. soln., so that benzoylation gives benzanilide, hexagonal plates, m.p. 163°.

65° *m*-Acetotoluidide, $CH_3{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_3$.

Oxidation ($KMnO_4$—1 hr.) ⟶ *m*-acetoamidobenzoic acid, needles, m.p. 248°.

72° *m*-Chloracetanilide, $Cl{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_3$.

87° *o*-Chloracetanilide, $Cl{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_3$.

88° *m*-Bromacetanilide, $Br{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_3$.

m.p.
94° *o*-Nitracetanilide, $NO_2 \cdot C_6H_4 \cdot NH \cdot CO \cdot CH_3$.
94° *o*-Nitrobenzanilide, $NO_2 \cdot C_6H_4 \cdot NH \cdot CO \cdot C_6H_5$.
99° *o*-Chlorobenzanilide, $Cl \cdot C_6H_4 \cdot NH \cdot CO \cdot C_6H_5$.
102° 2-Benzamidodiphenyl $C_6H_5 \cdot C_6H_4 \cdot NH \cdot CO \cdot C_6H_5$.
109° *o*-Iodoacetanilide, $I \cdot C_6H_4 \cdot NH \cdot CO \cdot CH_3$.
112° *o*-Acetotoluidide, $CH_3 \cdot C_6H_4 \cdot NH \cdot CO \cdot CH_3$.
Oxidation ($KMnO_4$—1 hr.) ⟶ 2-acetoamidobenzoic acid, needles, m.p. 185°.
114° Acetanilide, $C_6H_5 \cdot NH \cdot CO \cdot CH_3$.
Bromination (acetic acid) ⟶ *p*-bromacetanilide, prisms (aq. alcohol), m.p. 168°.
116° *o*-Bromobenzanilide, $Br \cdot C_6H_4 \cdot NH \cdot CO \cdot C_6H_5$.
117° Phenylacetanilide, $C_6H_5 \cdot CH_2 \cdot CO \cdot NH \cdot C_6H_5$.
119° 2-Acetamidodiphenyl, $C_6H_5 \cdot C_6H_4 \cdot NH \cdot CO \cdot CH_3$.
120° *m*-Bromobenzanilide, $Br \cdot C_6H_4 \cdot NH \cdot CO \cdot C_6H_5$.
120° 2 : 5-Dichlorobenzanilide.
121° *m*-Chlorobenzanilide, $Cl \cdot C_6H_4 \cdot NH \cdot CO \cdot C_6H_5$.
125° *m*-Benzotoluidide, $CH_3 \cdot C_6H_4 \cdot NH \cdot CO \cdot C_6H_5$.
136° 2-Acetnaphthalide, $C_{10}H_7 \cdot NH \cdot CO \cdot CH_3$.
137° *m*-Bromobenzanilide, $Br \cdot C_6H_4 \cdot CO \cdot NH \cdot C_6H_5$.
139° *o*-Iodobenzanilide, $I \cdot C_6H_4 \cdot NH \cdot CO \cdot C_6H_5$.
135° Phenacetine, $C_2H_5O \cdot C_6H_4 \cdot NH \cdot CO \cdot CH_3$.
Nitration: phenacetine (0·2 g.) is boiled for 30 secs. with conc. HNO_3 (1 c.c.) and water (4 c.c.). On pouring into water, 2-nitro-4-ethoxy-acetanilide is obtained. Orange prisms, m.p. 103°.
142° *o*-Benzotoluidide, $CH_3 \cdot C_6H_4 \cdot NH \cdot CO \cdot C_6H_5$.
147° 2 : 4-Dichloracetanilide.
147° Phenylurea, $C_6H_5 \cdot NH \cdot CO \cdot NH_2$.
Acetyl derivative: needles (aq. alcohol), m.p. 186°.
153° *p*-Acetotoluidide, $CH_3 \cdot C_6H_4 \cdot NH \cdot CO \cdot CH_3$.
Oxidation ($KMnO_4$—1 hr.) ⟶ *p*-acetamidobenzoic acid, needles, m.p. 250°.
155° *m*-Nitrobenzanilide, $NO_2 \cdot C_6H_4 \cdot NH \cdot CO \cdot C_6H_5$.
155° *m*-Nitracetanilide, $NO_2 \cdot C_6H_4 \cdot NH \cdot CO \cdot CH_3$.
158° *p*-Benzotoluidide, $CH_3 \cdot C_6H_4 \cdot NH \cdot CO \cdot C_6H_5$.
160° 1-Acetnaphthalide, $C_{10}H_7 \cdot NH \cdot CO \cdot CH_3$.

m.p.

163° Benzanilide, $C_6H_5 \cdot NH \cdot CO \cdot C_6H_5$.

Bromination (acetic acid) ⟶ *p*-bromobenzanilide: hexagonal plates, m.p. 204°.

162° 2-Benznaphthalide, $C_{10}H_7 \cdot NH \cdot CO \cdot C_6H_5$.

168° *p*-Bromacetanilide, $Br \cdot C_6H_4 \cdot NH \cdot CO \cdot CH_3$.

Dimorphous. When crystallised from alcohol elongated prisms are obtained, which, on standing over-night in contact with the mother-liquor, are converted into cubic prisms.

Nitration (fuming HNO_3 and acetic acid) ⟶ 2-nitro-compound, prisms, m.p. 106°.

169° 1-Benznaphthalide, $C_{10}H_7 \cdot NH \cdot CO \cdot C_6H_5$.

171° 4-Acetamidodiphenyl, $C_6H_5 \cdot C_6H_4 \cdot NH \cdot CO \cdot CH_3$.

179° *p*-Chloracetanilide, $Cl \cdot C_6H_4 \cdot NH \cdot CO \cdot CH_3$.

183° *p*-Iodoacetanilide, $I \cdot C_6H_4 \cdot NH \cdot CO \cdot CH_3$.

190° 4-Nitro-1-acetnaphthalide.

193° *p*-Chlorobenzanilide, $Cl \cdot C_6H_4 \cdot NH \cdot CO \cdot C_6H_5$.

199° 2-Nitro-1-acetnaphthalide.

199° *p*-Nitrobenzanilide, $NO_2 \cdot C_6H_4 \cdot NH \cdot CO \cdot C_6H_5$.

204° *p*-Bromobenzanilide, $Br \cdot C_6H_4 \cdot NH \cdot CO \cdot C_6H_5$.

206° Benzo-mesidide.

216° Acetomesidide.

216° *p*-Nitracetanilide, $NO_2 \cdot C_6H_4 \cdot NH \cdot CO \cdot CH_3$.

224° 1-Nitro-2-benznaphthalide.

222° *p*-Iodobenzanilide, $I \cdot C_6H_4 \cdot NH \cdot CO \cdot C_6H_5$.

238° *sym.*-Diphenylurea, $CO<\begin{matrix} NH \cdot C_6H_5 \\ NH \cdot C_6H_5 \end{matrix}$

Monoacetyl derivative: m.p. 106°.

257° Oxanilide, $C_6H_5 \cdot NH \cdot CO \cdot CO \cdot NH \cdot C_6H_5$.

Nitration (fuming HNO_3 and acetic acid) ⟶ di-*p*-nitro-compound, m.p. 260°,(mixed m.p., cf. m.p. of oxanilide).

Amino Acids

(General tests, see p. 75. Colour tests, see p. 42)

126° *N*-Phenylglycine, $C_6H_5 \cdot NH \cdot CH_2 \cdot COOH$.

Acetyl derivative: m.p. 194°.

Benzoyl derivative: m.p. 63°.

m.p.

145° Anthranilic acid, $NH_2 \cdot C_6H_4 \cdot COOH$.
Sublimes. Fluoresces in alcoholic soln.
Acetyl derivative: plates, m.p. 185°.
Bromination (acetic acid) ⟶ 3 : 5-dibromo-2-aminobenzoic acid, needles, m.p. 227°.
p-Nitrobenzyl ester: yellow cubic prisms, m.p. 210° (d).

174° *m*-Aminobenzoic acid, $NH_2 \cdot C_6H_4 \cdot COOH$.
Sublimes with some decomposition.
Acetyl derivative: needles (aq. alcohol), m.p. 250°: cf. m.p. of acetyl derivative of *p*-aminobenzoic acid.
p-Nitrobenzyl ester: m.p. 201°.

186° *p*-Aminobenzoic acid, $NH_2 \cdot C_6H_4 \cdot COOH$.
Acetyl derivative: m.p. 257°: cf. acetyl derivative of *m*-aminobenzoic acid.

190° Hippuric acid, $C_6H_5 \cdot CO \cdot NH \cdot CH_2 \cdot COOH$.
p-Nitrobenzyl ester: elongated prisms, m.p. 136°.
Sodium salt gives a buff-coloured ppt. with $FeCl_3$.

224–225° *d*-Glutamic acid, $COOH \cdot CH_2 \cdot CH_2 \cdot CH(NH_2) \cdot COOH$.
Benzoyl derivative: m.p. 138°.

226° *l*-Asparagine, $COOH \cdot CH(NH_2) \cdot CH_2 \cdot CO \cdot NH_2$.
Crystallises with one mol. of water which is lost at 100°.
p-Toluenesulphonyl derivative: prisms, m.p. 195°.
Picrate: yellow prisms, decompose at 185°.

232–236° Glycine, $NH_2 \cdot CH_2 \cdot COOH$.
Sweet taste.
$FeCl_3$: reddish-brown coloration.
p-Toluenesulphonyl derivative: prisms or needles, m.p. 147°.
Picrate: long yellow plates, m.p. 201° (d).
Picrolonate: yellow prisms, m.p. about 245° (d).

238° *d*-Arginine, $\genfrac{}{}{0pt}{}{NH}{NH_2}\!>\!C \cdot NH \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH(NH_2) \cdot COOH$.
Picrate: yellow, m.p. 217°.
Picrolonate: yellow, m.p. 225°.

271° (sealed tube) *l*-Aspartic acid, $COOH \cdot CH_2 \cdot CH(NH_2) \cdot COOH$.
Reduces Fehling's solution.
Benzoyl derivative: m.p. 185°.

m.p.

285° Histidine, $C_6H_9O_2N_3$.
p-Toluenesulphonyl derivative: prisms, m.p. 202–204°.
Picrolonate: yellow prisms, m.p. 220°.

294° (d) *l*-Leucine, $(CH_3)_2CH{\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOH$.
Picrolonate: yellow prisms, m.p. 145–150° (d).

297° *l*-Alanine, $CH_3{\cdot}CH(NH_2){\cdot}COOH$.
Sweet taste.
p-Toluenesulphonyl derivative: elongated prisms (aq. alcohol), m.p. 132°.
p-Nitrobenzyl derivative: prisms, m.p. 228–230°.

310° (d) *l*-Tyrosine, $HO{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOH$.
H_2SO_4 (warming) ⟶ red coloration.
p-Toluenesulphonyl derivative: elongated prisms (aq. alcohol), m.p. 117°.
Picrolonate: yellow prisms, m.p. 260° (d).

Phenylhydrazines

(General tests, see p. 76)

Liquids

b.p.

227° *Unsym.*-Methylphenylhydrazine, $\genfrac{}{}{0pt}{}{C_6H_5}{CH_3}{>}N{\cdot}NH_2$.
Benzaldehyde ⟶ hydrazone, prisms, m.p. 106°.

243° Phenylhydrazine, $C_6H_5{\cdot}NH{\cdot}NH_2$.
Benzaldehyde ⟶ hydrazone, prisms, m.p. 156°.

145° 20 mm. *m*-Tolylhydrazine, $CH_3{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2$.
Acetophenone ⟶ hydrazone, long prisms, m.p. 81°.

Solids

m.p.

60° *o*-Tolylhydrazine, $CH_3{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2$.
Acetophenone ⟶ hydrazone, prisms, m.p. 101°.

66° *p*-Tolylhydrazine, $CH_3{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2$.
Acetophenone ⟶ hydrazone, leaflets, m.p. 125°.

116° α-Naphthylhydrazine, $C_{10}H_7{\cdot}NH{\cdot}NH_2$.
Benzaldehyde ⟶ hydrazone, needles or plates, m.p. 144°.

m.p.

125° β-Naphthylhydrazine, $C_{10}H_7{\cdot}NH{\cdot}NH_2$.
Benzaldehyde ⟶ hydrazone, plates, m.p. 192°.

106° *p*-Bromophenylhydrazine, $Br{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2$.
Benzaldehyde ⟶ hydrazone, plates, m.p. 127°.

157° *p*-Nitrophenylhydrazine, $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2$.
Orange-red.
Benzaldehyde ⟶ hydrazone, orange-red needles, m.p. 190°.

194° 2 : 4-Dinitrophenylhydrazine.
Red.
Acetone ⟶ hydrazone, yellow prisms, m.p. 126°.

Nitroso, Azoxy, Hydrazo, and Azo Compounds

(General tests, see pp. 76–77)

Solids

36° Azoxybenzene, $C_6H_5{\cdot}\underset{\underset{O}{\|}}{N}{:}N{\cdot}C_6H_5$.
Pale yellow.
Reduction (Zn dust, NaOH, and alcohol) ⟶ azobenzene, orange plates, m.p. 68°.

55° *o*-Azotoluene, $CH_3{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4{\cdot}CH_3$.
Red.
Reduction (Zn dust, NaOH, and alcohol) ⟶ *o*-hydrazotoluene, plates, m.p. 165°.

59° *o*-Azoxytoluene, $CH_3{\cdot}C_6H_4{\cdot}\underset{\underset{O}{\|}}{N}{:}N{\cdot}C_6H_4{\cdot}CH_3$.
Pale yellow.
Reduction (Zn dust, NaOH, and alcohol) ⟶ *o*-azotoluene, orange plates, m.p. 55°.

68° Nitrosobenzene, $C_6H_5{\cdot}NO$.
Colourless. Green in solution or fused state.
Sharp odour.
Aniline (in acetic acid) ⟶ azobenzene, orange-red plates, m.p. 68°.

m.p.

68° Azobenzene, $C_6H_5 \cdot N{:}N \cdot C_6H_5$.
Orange-red.
Reduction (Zn dust, NaOH, and alcohol) ⟶ hydrazobenzene, plates, m.p. 130°.

75° *p*-Azoxytoluene, $CH_3 \cdot C_6H_4 \cdot \underset{\underset{O}{\uparrow\downarrow}}{N}{:}N \cdot C_6H_4 \cdot CH_3$.
Pale yellow.
Reduction (Zn dust, NaOH, and alcohol) ⟶ *p*-hydrazotoluene, orange plates, m.p. 129°.

84° *p*-Nitrosodiethylaniline, $(C_2H_5)_2N \cdot C_6H_4 \cdot NO$.
Dark green.

87° *p*-Nitrosodimethylaniline, $(CH_3)_2N \cdot C_6H_4 \cdot NO$.
Dark green.

126° *p*-Aminoazobenzene, $C_6H_5 \cdot N{:}N \cdot C_6H_4 \cdot NH_2$.
Yellow. Yellow colour with H_2SO_4.
Benzoyl derivative: hexagonal plates (acetic acid), m.p. 205°.
Acetyl derivative: m.p. 144°.

134° Benzeneazo-β-naphthol, $HO \cdot C_{10}H_6 \cdot N{:}N \cdot C_6H_5$.
Red. Magenta colour with H_2SO_4.
Acetyl derivative: m.p. 117°.

144° *p*-Azotoluene, $CH_3 \cdot C_6H_4 \cdot N{:}N \cdot C_6H_4 \cdot CH_3$.
Orange.
Reduction (Zn dust, NaOH, and alcohol) ⟶ *p*-hydrazotoluene, plates, m.p. 129°.

130° Hydrazobenzene, $C_6H_5 \cdot NH \cdot NH \cdot C_6H_5$.
Colourless. Easily oxidised by the air to azobenzene.
Reduces warm Fehling's solution.
On standing overnight with an alcoholic soln. of phenyl *iso*thiocyanate a derivative is obtained, prisms, m.p. 173°.

152° *p*-Hydroxyazobenzene, $C_6H_5 \cdot N{:}N \cdot C_6H_4 \cdot OH$.
Yellow.
Benzoyl derivative: m.p. 138°.

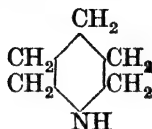
Heterocyclic Compounds

(General tests, see pp. 77–78)

Liquids

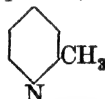
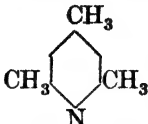
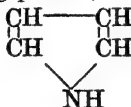
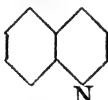
b.p.

106° Piperidine,

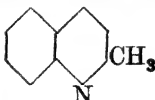
CH_2
CH_2 CH_2
CH_2 CH_2
NH

Unpleasant ammoniacal odour. Fumes in air. Miscible with water giving alkaline soln.
HCl salt : needles (alcohol–ether), m.p. 249°.
Picrate : yellow needles, m.p. 151°.
p-Toluenesulphonyl derivative : prisms, m.p. 104°.

116° Pyridine,

Characteristic odour. Miscible with water.
Picrate : orange needles, m.p. 167°.
Methiodide : long prisms, m.p. 117°.

129° α-Picoline,

Odour like that of pyridine.
Picrate : yellow needles, m.p. 169°.
Methiodide : long prisms, m.p. 224°.

131° Pyrrole,

Generally has unpleasant odour. Darkens on exposure to the air.
Pine-splint test : a pine-splint moistened with HCl assumes a red colour when exposed to the vapour of pyrrole.
Isatin reaction : a small quantity of isatin is dissolved in H_2SO_4 (1 c.c.) and water (10 c.c.) is added. This soln. when cold gives a blue ppt. with pyrrole.

b.p.

171° 2 : 4 : 6-Trimethylpyridine, CH_3 CH_3 CH_3 N

Picrate : yellow needles, m.p. 156°.

237° Quinoline, N

Characteristic odour. Volatile in steam.

Picrate : yellow elongated needles (acetic acid), m.p. 205°.

Methiodide : yellow prisms with indistinct m.p.

247° Quinaldine,

Odour like quinoline.

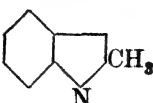
HCl salt : m.p. 218°.

Picrate : yellow plates, m.p. 193°.

Methiodide : not so readily prepared as that of quinoline.

242° Isoquinoline,

M.p. 25°.

Picrate : yellow prisms, m.p. 223°.

Methiodide : pale yellow plates, m.p. 159°.

241° *l*-Nicotine, $C_{10}H_{14}N_2$.

Miscible with water.

Picrate : purified by washing with benzene, m.p. 217°.

Solids

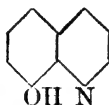
m.p.

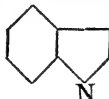
61° 2-Methylindole,

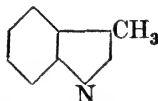
Picrate : brick-red needles, m.p. 139°.

m.p.

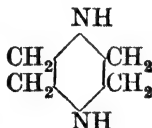
75–76° 8-Hydroxyquinoline,

OH N

Volatile in steam. Saffron-like odour.
$FeCl_3$: intense green (water).
Benzoyl derivative: hexagonal prisms, m.p. 119°.

52° Indole,

Volatile in steam.
Picrate: red needles (benzene), m.p. 163°.

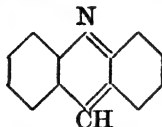
95° Skatole,

Pine-splint test negative.
Intolerable odour. Volatile in steam.
H_2SO_4 (heat) ⟶ red colour.
Picrate: red needles (benzene), m.p. 172–173°.

104° Piperazine,

NH
CH_2 CH_2
CH_2 CH_2
NH

b.p. 140°.

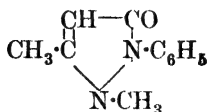
Soluble in water.
Dibenzoyl derivative: plates, m.p. 194°.
Acetic acid salt: needles, m.p. 217°.
Picrate: yellow needles, m.p. 280°.

110° Acridine,

N
CH

Colourless when pure. Sublimes. Volatile in steam.
Blue fluorescence in very dilute soln.
Picrate: yellow needles (acetic acid), m.p. about 208°.

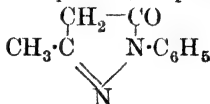
m.p.

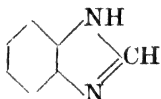
113° Antipyrine,

$$\begin{array}{c} CH{-}CO \\ CH_3{\cdot}C \quad N{\cdot}C_6H_5 \\ N{\cdot}CH_3 \end{array}$$

$FeCl_3$: blood-red colour (water).
Picrate : yellow needles, m.p. 188°.

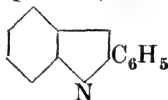
124° (d) Picrolonic acid, (formula, see p. 72).
Diethylamine picrolonate : yellow prisms, m.p. 262°.

127° 1-Phenyl-3-methyl-5-pyrazolone,

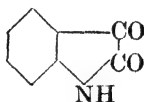
$$\begin{array}{c} CH_2{-}CO \\ CH_3{\cdot}C \quad N{\cdot}C_6H_5 \\ N \end{array}$$

$FeCl_3$: red colour (alcohol).
Bromination (acetic acid) ⟶ dibromo-compound, m.p. 80°.

170° Benziminazole,

Picrate : yellow prisms (acetic acid), m.p. 230°.

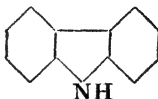
189° 2-Phenylindole,

C_6H_5
N

Sublimes.
Slightly volatile in steam.
Picrate : red, m.p. 127°.
3-*Iso*nitroso-compound : yellow needles (amyl acetate), m.p. 280°.

203° Isatin,

CO
CO
NH

Red.
Dissolves in sodium hydroxide giving first a violet and finally a red colour.

245° Carbazole,

NH

m.p.

Sublimes.
$H_2SO_4 \longrightarrow$ yellow colour.
Picrate : orange needles, m.p. 183°.

(d) Hexamethylenetetramine, $(CH_2)_6N_4$.
Picrate : yellow prisms, m.p. 188°.

Aromatic Sulphonic Acids

(General tests, see pp. 78–79)

Solids

48° *m*-Nitrobenzenesulphonic acid, $NO_2{\cdot}C_6H_4{\cdot}SO_3H$.
Aniline salt : plates (water), m.p. 215° (d).
Amide : needles, m.p. 162°.
Pseudobenzylthiourea salt : prisms, m p. 140°.

57° *o*-Toluenesulphonic acid, $C_6H_4\!<\!\begin{smallmatrix}CH_3\\SO_3H\end{smallmatrix}$
Hygroscopic.
Aniline salt : needles, m.p. 222°.
Amide : plates, m.p. 153°.
Pseudobenzylthiourea salt : prisms, m.p. 178°.

65° Benzenesulphonic acid, $C_6H_5{\cdot}SO_3H$.
Hygroscopic.
Amide : plates, m.p. 156°.
Pseudobenzylthiourea salt : needles or plates, m.p. 144°.

70° *o*-Nitrobenzenesulphonic acid, $C_6H_4\!<\!\begin{smallmatrix}SO_3H\\NO_2\end{smallmatrix}$
Amide : needles, m.p. 188°.
Pseudobenzylthiourea salt : m.p. above 280°.

90° *α*-Naphthalenesulphonic acid, $C_{10}H_7{\cdot}SO_3H$.
Amide : plates, m.p. 150°.
Pseudobenzylthiourea salt : m.p. 136°.

92° *p*-Toluenesulphonic acid, $CH_3{\cdot}C_6H_4{\cdot}SO_3H$.
Hygroscopic.
Aniline salt : needles, m.p. 225°.
Amide : plates, m.p. 137°.
Pseudobenzylthiourea salt : plates, m.p. 178°.

124° β-Naphthalenesulphonic acid, $C_{10}H_7{\cdot}SO_3H$.
Amide : m.p. 212°.
Pseudobenzylthiourea salt : needles, m.p. 188°.

SUBSTITUTED SULPHONIC ACIDS

m.p.

p-Phenolsulphonic acid, $HO \cdot C_6H_4 \cdot SO_3H$.
Hygroscopic liquid.
Bromine water (heating) ⟶ *sym.*-tribromophenol, needles, m.p. 119°.

2-Naphthol-3 : 6-disulphonic acid.
Deliquescent crystals. Blue fluorescence in ammonia soln.
$FeCl_3$: blue (water).
Aniline salt : elongated prisms (water), m.p. 225°.

(d) 2-Naphthol-6 : 8-disulphonic acid.
Deliquescent crystals.

(d) 2 : 7-Naphthalenedisulphonic acid.
Hygroscopic needles.
Aniline salt : needles (water), m.p. 251 2°.
Diamide : plates, m.p. 242°.
Pseudobenzylthiourea salt : plates, m.p. 205°.

(d) 2 : 6-Naphthalenedisulphonic acid.
Hygroscopic crystals.
Amide : m.p. above 300°.
Pseudobenzylthiourea salt : decomposes at 200°.

(d) 2 : 5-Dichlorobenzenesulphonic acid, $C_6H_3 \begin{cases} SO_3H & (1) \\ Cl & (2) \\ Cl & (5) \end{cases}$
Pseudobenzylthiourea salt : plates, m.p. 170°.

120° Sulphosalicylic acid, $C_6H_3(COOH)(OH)(SO_3H)$ [ring formula: COOH, OH, SO_3H]
Very soluble in water, and is consequently easily distinguished from salicylic acid.
$FeCl_3$: magenta colour.

125° 2-Naphthol-6-sulphonic acid.
$FeCl_3$: blue (water).
Blue fluorescence in water when ammonia is added.

134° *o*-Sulphobenzoic acid, $COOH \cdot C_6H_4 \cdot SO_3H$.

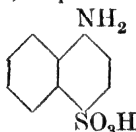
m.p.

141° *m*-Sulphobenzoic acid, $SO_3H{\cdot}C_6H_4{\cdot}COOH$.
Aniline salt : m.p. 233°.

170° 1-Naphthol-4-sulphonic acid.
approx. $FeCl_3$. blue colour.

259° *p*-Sulphobenzoic acid, $SO_3H{\cdot}C_6H_4{\cdot}COOH$.
Diamide : needles (water), m.p. 230°.

(d) Metanilic acid, $NH_2{\cdot}C_6H_4{\cdot}SO_3H$ (1 : 3).
Amide : needles, m.p. 142°.
N-Acetyl derivative : m.p. 217°.

(d) Sulphanilic acid, $NH_2{\cdot}C_6H_4{\cdot}SO_3H$ (1 : 4).
Bromine (acetic acid) ⟶ *sym.*-tribromaniline : purified by washing with dil. HCl and crystallisation from alcohol : prisms, m.p. 119°.

(d) Naphthionic acid, [naphthalene ring with NH_2 at position 1 and SO_3H at position 4]
Blue fluorescence in ammonia solution.

Sulphonyl Chlorides

(General tests, see p. 79)

Liquids

b.p.

135°/15 mm. *o*-Toluenesulphonyl chloride, $CH_3{\cdot}C_6H_4{\cdot}SO_2Cl$, m.p. 10°.
Characteristic odour.
Amide : plates, m.p. 153°.

251° Benzenesulphonyl chloride, $C_6H_5{\cdot}SO_2{\cdot}Cl$.
Characteristic odour.
Amide : plates, m.p. 156°.
Anilide : octahedra (aq. alcohol), m.p. 112°.

Solids

m.p.

60° *m*-Nitrobenzenesulphonyl chloride, $NO_2{\cdot}C_6H_4{\cdot}SO_2Cl$.
Amide : needles, m.p. 162°.

68° α-Naphthalenesulphonyl chloride, $C_{10}H_7{\cdot}SO_2{\cdot}Cl$.
Amide : plates, m.p. 150°.

m.p.

69° *p*-Toluenesulphonyl chloride, $CH_3 \cdot C_6H_4 \cdot SO_2 \cdot Cl$.
Amide: plates, m.p. 137°.

76° β-Naphthalenesulphonyl chloride, $C_{10}H_7 \cdot SO_2 \cdot Cl$.
Amide: plates, m.p. 212°.

Sulphonamides

(General tests, see p. 79)

Solids

137° *p*-Toluenesulphonamide, $CH_3 \cdot C_6H_4 \cdot SO_2 \cdot NH_2$.
Benzyl derivative: m.p. 116°.

150° α-Naphthalenesulphonamide, $C_{10}H_7 \cdot SO_2 \cdot NH_2$.
Benzyl derivative: m.p. 137°.

156° Benzenesulphonamide, $C_6H_5 \cdot SO_2 \cdot NH_2$.
Benzyl derivative: m.p. 88°.

153° *o*-Toluenesulphonamide, $CH_3 \cdot C_6H_4 \cdot SO_2 \cdot NH_2$.

212° β-Naphthalenesulphonamide, $C_{10}H_7 \cdot SO_2 \cdot NH_2$.
Benzyl derivative: m.p. 124°.

220° *o*-Sulphobenzoic imide.
(d) Sodium derivative is known as saccharin, which has an extremely sweet taste.
Benzyl derivative: m.p. 118°.

Thioamides

(General tests, see p. 79)

Solids

154° Phenylthiourea, $C_6H_5 \cdot NH \cdot CS \cdot NH_2$.
$CH_3I \longrightarrow$ *S*-Methyl-*N*-phenyl*iso*thiourea: picrate, yellow plates, m.p. 175°.

180° Thiourea, $NH_2 \cdot CS \cdot NH_2$.
Picrate (prepared in acetic acid): insoluble in boiling alcohol, high m.p.
Monoacetyl derivative: sq. prisms (water), m.p. 165°.
Alkyl*iso*thioureas: see p. 92.

m.p.

182° Thiosemicarbazide, $NH_2 \cdot CS \cdot NH \cdot NH_2$.
Acetyl derivative : m.p. 165°.
Acetone thiosemicarbazone : m.p. 179°.

*Iso*THIOCYANATES

(General tests, see p. 79)

Liquids

b.p.

220° Phenyl *iso*thiocyanate, $C_6H_5N{:}C{:}S$.
Sharp odour.
Aniline ⟶ thiocarbanilide, plates (acetic acid), m.p. 153°.

239° *o*-Tolyl *iso*thiocyanate, $C_6H_4{<}{}^{CH_3}_{N:C:S}$
Sharp odour.
Aniline ⟶ substituted thiourea, needles, m.p. 139°.

239° *p*-Tolyl *iso*thiocyanate, $CH_3 \cdot C_6H_4 \cdot N{:}C{:}S$, m.p. 26°.
Aniline ⟶ substituted thiourea, prisms (aq. alcohol), m.p. 141°.

Solids

m.p.

45–7° *p*-Chlorophenyl *iso*thiocyanate, $Cl \cdot C_6H_4 \cdot N{:}C{:}S$.
Aniline ⟶ substituted thiourea, plates, m.p. 152°.

58° α-Naphthyl *iso*thiocyanate, $C_{10}H_7 \cdot N{:}C{:}S$.
Aniline ⟶ substituted thiourea, plates, m.p. 158°.

60° *m*-Nitrophenyl *iso*thiocyanate, $NO_2 \cdot C_6H_4 \cdot N{:}C{:}S$.
Aniline ⟶ substituted thiourea, needles, m.p. 155°.

62° β-Naphthyl *iso*thiocyanate, $C_{10}H_7 \cdot N{:}C{:}S$.
Aniline ⟶ substituted thiourea, plates, m.p. 182°.

70° 4-Diphenylyl *iso*thiocyanate, $C_6H_5 \cdot C_6H_4 \cdot N{:}C{:}S$.
Methylamine ⟶ substituted thiourea, needles, m.p. 142°.

Bibliography

Reference Books

Beilstein : *Organische Chemie.*
Heilbron : *Dictionary of Organic Compounds.*

Authoritative Books on Qualitative Organic Chemistry

Mulliken : *Identification of Pure Organic Compounds.*
Meyer, Hans : *Nachweis und Bestimmung organischer Verbindungen.*
Meyer, Hans : *Analyse und Konstitutionsermittlung organischer Verbindungen.*
Allen : *Commercial Organic Analysis.*
Rosenthaler : *Der Nachweis organischer Verbindungen.*
Ekkert : *Erkennung organischer Verbindungen.*

Student Textbooks

Clarke : *Handbook of Organic Analysis.*
Weston : *Carbon Compounds.*
Thorpe and Whitley : *Organic Chemical Analysis.*
Shriner and Fuson : *Identification of Organic Compounds.*
Kamm : *Qualitative Organic Analysis.*
Hawk : *Practical Physiological Chemistry.*
Plimmer : *Practical Organic and Biochemistry.*
Storrie : *Notes on Qualitative Organic Analysis.*

Physical Data

International Critical Tables.
Vogel and Georg : *Tabellen der Zucker und ihrer Derivate.*
Hodgman : *Handbook of Chemistry and Physics.*

Apparatus

Houben-Weyl : *Methoden der organischen Chemie.*
Findlay : *Practical Physical Chemistry.*
Bernhauer : *Einführung in die organisch-chemische Laboratoriumstechnik.*
Morton : *Laboratory Technique in Organic Chemistry.*

Special Topics

Kofler and Kofler : *Mikroskopische Methoden in der Mikrochemie.*
Hartshorne and Stuart : *Crystals and the Polarising Microscope.*
Zechmeister and Cholnoky : *Die Chromatographische Adsorptionsmethode.*
Radley and Grant : *Fluorescence Analysis in Ultra-violet Light.*
Danckwortt : *Lumineszenz-Analyse im filtrierten Ultravioletten Licht.*

Journals

The Analyst.
Zeitschrift für Analytische Chemie.
Industrial and Engineering Chemistry. Analytical Edition.
Mikrochemie.

Many other journals contain papers on qualitative chemistry.

Preparation of Special Reagents

Barfoed's Reagent. Crystalline copper acetate (9 g.) is dissolved in water (100 c.c.), and 50% acetic acid (1·2 c.c.) is added. It is advisable to use freshly prepared reagent for testing purposes.

Bial's Orcinol Reagent. Orcinol (1·5 g.) is dissolved in concentrated hydrochloric acid (500 g.), and 20–30 drops of 10% ferric chloride solution are added.

Dinitrophenylhydrazine Reagent. *Allen's Method.* Dinitrophenylhydrazine (5 g.) is finely powdered and boiled under reflux for 5 mins. with alcohol (500 c.c.). The solution is cooled rapidly, and a suspension of small crystals is obtained. Before use the suspension should be well shaken.

Fehling's Solution. Two solutions are made, one by dissolving 70 g. of crystalline cupric sulphate in water (1000 c.c.), and the other by dissolving 350 g. of Rochelle Salt (sodium potassium tartrate) and sodium hydroxide (100 g.) in 1000 c.c. of water. Fehling's solution is obtained by mixing equal volumes of the two solutions. The two solutions are generally bottled separately and mixed just before use, as Fehling's solution does not "keep" well.

Ferric Chloride Solution. This generally contains a considerable quantity of hydrochloric acid, and is unsuitable for many reactions. The "neutral" solution is made by adding dilute sodium hydroxide solution until a small permanent precipitate of ferric hydroxide is obtained, and filtering the solution. The solution so obtained is not quite neutral, but is suitable for tests.

Millon's Reagent. Mercury (10 g.) is dissolved in 20 g. concentrated nitric acid (1·42), and the solution is then diluted with 30 c.c. of water. Any precipitate formed is allowed to settle, and the clear solution is decanted.

Schiff's Reagent. Rosaniline (0·1 g.) is dissolved in water (100 c.c.) and the solution is filtered and mixed with an equal volume of water saturated with sulphur dioxide. The solution is allowed to stand for several hours, and if the pink colour reappears a few drops of water containing sulphur dioxide are added. The reagent keeps well if kept in a dark-coloured bottle.

Seliwanoff's Reagent. Resorcinol (0·1 g.) is dissolved in 100 c.c. of dilute hydrochloric acid (1 part concentrated hydrochloric acid and 2 parts water).

GENERAL INDEX

Numbers in heavy type refer to pages on which experimental directions are given.

INDEX OF AUTHORS' NAMES

LIST OF COMPOUNDS GIVEN IN PART B